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Mechanisms of cyanide attenuation in soils

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Mechanisms of Cyanide Attenuation in Soils

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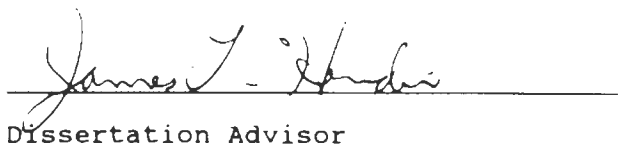

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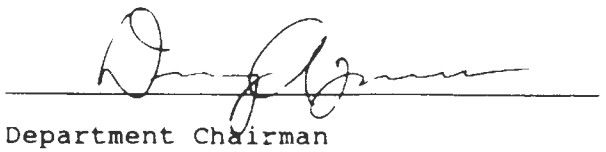

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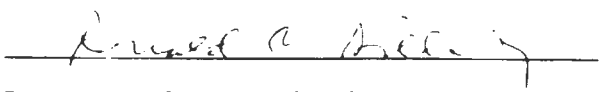

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ABSTRACT

Three types of tests, stirred reactor, tall column, and large tank, were run to identify the mechanisms of cyanide attenuation in soils. Ten pure minerals which comprise the major part of soils were tested. Minerals with high content of alumina are found to attenuate cyanide in an appreciable amount through adsorption. Calcareous and silicous minerals do not tend to react with cyanide. Six major mechanisms of cyanide attenuation in soils were identified. They are adsorption/ion exchange, complexation, oxidation, precipitation, volatilization, and transformation to nitrate.

Oxidation is found to be a catalytic process with metal cyanide complexes, $[Ni(CN)_4]^{2-}$ and $[Cu(CN)_4]^{3-}$, being the catalysts. Precipitation of metal cyanide complexes occurs usually at low pH, 3-9 for $Zn(CN)_{2(s)}$ and 2-8 for $Cd(CN)_{2(s)}$. Iron existing as hematite in soils does not react with cyanide.

The attenuation of cyanide in pure minerals is mainly an adsorption process with a first-order rate. pH is a key factor for volatilization, adsorption/ion exchange and precipitation processes, all of which were enhanced at low pH values.

Zinc, either existing in the soils originally or added to the fresh

cyanide solutons was completely precipitated in the soils. Nickel, and copper in the effluent were found to be complexed with CN^-. A mass balance on CN^- showed that 33.6% cyanide originally added was attenuated by transformation to nitrate, 11.7% by adsorption, 7.3% by precipitation, 4.2% by oxidation, 5-13% by volatilization, and 4% by complexing. About 26% cyanide was attenuated through unidentified mechanisms.

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INTRODUCTION

The successful dissolution of gold in cyanide solution was carried out as early as 1843, and the commercial application of cyanide in gold extraction dates back to 1889. Since then cyanidation has dominated the precious metal industry for nearly a century. The use of cyanide has dramatically expanded with the rapid recent increase in cyanide heap leaching technology for processing low grade gold ores. Not only has cyanide been used in precious metal and chemical industries, but it is also produced as a waste product in many other industrial processes such as steel making and coal gasification. Cyanide is also largely used in electroplating of metals. It is worth noting that there is no recognized replacement for cyanide in precious metal leaching in the foreseeable future.

In 1980, when Congress amended the Resource Conservation and Recovery Act, it instructed EPA to conduct a comprehensive study of the adverse effects on human health and environment, if any, of the disposal and utilization of mining wastes. Potential problems identified by EPA include mineral processing wastes containing cyanide. A major concern regarding the impact of cyanide on the environment is the possibility of ground water contamination by cyanide as a result of spills or leakage of cyanide wastes from mining operations.

Some work has been done on ground water monitoring in mining sites in recent years. In October 1982, Cortez Gold Mines started conducting field tests on ground water. Five monitoring wells were sampled and analyzed for cyanide(1). Initial results indicated that cyanide concentrations in all the wells were below 20 ppb which is considered safe. But later, they found some contaminated water in some monitoring wells(2,3) three to four miles from the tailings pond area. A pumpback well system was used for remediation of ground water contamination at the time(4,5). In August 1984 Cortez Gold Mines proposed to line the impoundment with selected soils of high clay content having an impermeability of 10^{-7} cm/sec(6).

In 1983, Cyprus Mines Corporation conducted some laboratory tests and engineering assessments to determine the feasibility of utilizing compacted in-situ natural soils as a liner material for proposed new emergency catch basins at the Northumberland Project(7). Their conclusion was that use of compacted site soils for liners is appropriate and results in significant savings in comparison to the installation of synthetic liners.

Du Pont Company has been monitoring and remediating ground water contamination by sodium cyanide leaks at the Carlin Terminals for nearly ten years(8,9). They found some warning signs of ground water contamination by cyanide in sample analyses from some monitoring wells. The remediation methods considered and tested are as follows: by allowing the cyanide to detoxify naturally in situ

by hydrolysis with ground water, by complexing with metals present in the soil, by self polymerization and by pumping contaminated water out of the ground for surface treatment.

In February 1982, a workshop on "Cyanide Effluents from Mineral Processing"(10) was held at the US Bureau of Mines, Salt Lake Research Center. The workshop focused on use of cyanide as it relates to the gold and silver mining industry and froth flotation processes employed by mineral mining companies. Its intent was to discuss state of the art technology and provide information pertinent to cyanide use in the minerals industry. The main topics of discussion included: the chemistry and use of cyanides, control and treatment of cyanide mining wastes, fate of cyanide in the environment and the analytical chemistry of cyanide. From the workshop discussion, the problems associated with cyanide use in the mining industry, and areas where technical information is insufficient were identified. The types of research required to understand and resolve potential adverse environmental problems were also identified. The problems identified are as follows: (a) the form in which cyanide occurs in flotation and cyanidation process tailings impoundments is not well known; (b) many of the processes used to treat effluents to remove cyanide require considerable retention times and may not be practical, or appropriate, to small operators; (c) the scope of the problems of cyanide toxicity cannot be limited to free cyanide in the broad perspective and in the real world; and (d) limited information is

available on the fate of cyanide from leaching and flotation operations in soils(10).

In December 1984, a conference entitled "Cyanide and the Environment" was held in Tucson, Arizona. While it appeared that considerable interest was generated in the period between these conferences little additional information was produced on the fate of cyanide from mining and mineral processing operations in soils.

Although many processes for cyanide removal and detoxication have been proposed, tested and used, there is a general lack of specific information on the environmental fate of cyanide in soil(11), particularly, the mechanisms of attenuation of cyanide in soils and forms of cyanide in soils. This information is necessary to predict the possibility of cyanide contamination of ground water through solution leaks from the operations in the precious metal industry. Besides, the universal presence of soil and its complex chemical and physical processes make it a potential waste degradation source. Therefore, a better understanding of cyanide in soil aids in the assessment of the potential risk of ground water contamination by cyanide, and permits the evaluation of the possible use of soil as a material for cyanide waste treatment.

The objectives of this study were to identify the chemical and physical mechanisms for soil to attenuate cyanide, to distinguish the important parameters and characteristics of soil for degrading

cyanide, and to study the pattern of cyanide movement in soils.

To accomplish the objectives three types of tests were designed. The first approach was testing major minerals in soil using stirred reactor tests so the promising minerals which attenuate cyanide could be identified. The second approach was a tall column test conducted to obtain a total mass balance for cyanide in soil by analyzing for all possible species of cyanide in the gas, solution and solid phases. The third approach was a large radius tank test run to study the vertical and radial movement and distribution of cyanide in soil and the effect of zinc on the process by analyzing gas samples from different concentric rings and solution samples taken from different radii and depths.

LITERATURE REVIEW

A. Cyanide Chemistry

Free Cyanide Free Cyanide includes hydrogen cyanide and simple cyanide salts. Hydrogen cyanide is a colorless gas or liquid with a boiling point of 25.7°C. HCN is a weak acid with a dissociation constant of $4.635*10^{-10}$ at 20°C for the equilibrium hydrolysis reaction between cyanide ion and water

$$CN^- + H_2O \rightleftharpoons HCN + OH^- \quad (1)$$

This reaction is strongly pH dependent as shown in Figure 1. Acid solutions favor the presence of HCN and, at pH values below 7 essentially all of the cyanide is present as HCN. At a pH of 9.36 the concentrations of HCN and CN^- are equal. In solution, HCN will also maintain equilibrium with atmospheric vapor. In solution, the concentration of gaseous HCN in water may be approximated by Henry's law relationship(K_h=4368 mmHg/mole fraction at 20°C). It is known that HCN can be removed from solution by volatilization which depends on pH, temperature, interfacial area and concentration. Hydrogen cyanide can be oxidized to cyanogen, $(CN)_2$, or cyanic acid(12).

Simple cyanide salts may be represented by the general formula $A(CN)_x$, where A is a cation(sodium, potassium, ammonium, etc.), and x the valance of A and represents the number of cyano groups present in the salt. Soluble compounds, particularly the alkali cyanides, ionize to release cyanide ions according to the reaction

$$A(CN)_x \rightleftharpoons A^{+x} + xCN^- \quad (2)$$

Lengthy heating of aqueous solutions results in their complete decomposition. On melting or boiling with sulphur or polysulfides, alkali cyanides change into the corresponding thiocyanates, for

example

$$NaCN + 1/2S_2 + H_2O \rightarrow HCNS + NaOH \quad (3)$$

If cyanides are heated when exposed to air, or if they are allowed to react with a readily reducible oxide, e.g. MnO_2 or $K(MnO_4)$, then they readily convert into cyanates

$$ACN + 1/2O_2 \underline{\text{heat}} AOCN \quad (4)$$

Passing chlorine into cyanide solutions causes formation of cyanogen chloride

$$NaCN + Cl_2 \rightarrow ClCN + NaCl \quad (5)$$

Bromine and iodine react similarly to form BrCN and ICN. At low temperatures SO_2 reacts with aqueous KCN or NaCN solution with formation of HCN and potassium or sodium cyanosulfite, KSO_2CN.

Sodium cyanide, NaCN, crystallizes from aqueous solution with one or two water molecules added, depending on the temperature. In aqueous sodium cyanide solution, many metals in a finely dispersed condition, except for Pt and Pb, are soluble in the presence of oxygen. NaCN dissolves readily in water and alcohol. In aqueous solution it reacts with sodium tetrathionate to form thiocyanate. Potassium cyanide, KCN, is obtained from water as an anhydrous

compound; it melts at 622°C, remaining unchanged in the presence of oxygen and moisture even at white heat. Its aqueous solutions can be stored for a limited time without contact with air; after a certain period of time KCN partially hydrolyzes with the formation of NH_3 and potassium formate. Ammonium cyanide, NH_4CN is a colorless, crystalline compound, and highly unstable on exposure to air and decomposes readily to produce NH_3 and HCN. Lithium cyanide, LiCN, has properties similar to those of sodium and potassium cyanide. It is readily soluble in water and remains unchanged when heated to elevated temperature.

Complex Formation Ability of the Cyanide Ion

Cyano Compounds of the p and d Block Elements

The cyanides of this group are colorless and diamagnetic; they are easily obtained by combining cyanide with solutions of the corresponding metal salt. While zinc cyanide is sparingly soluble in water($4.5*10^{-5}$ M/L) and ethanol, mercury cyanide is readily soluble in water and ethanol. The only known cyano complexes of zinc are those containing the $[Zn(CN)_4]^{2-}$ ion. Zinc cyanide is soluble in liquid ammonia. Cyano compounds of cadmium closely resemble those of zinc, but cadmium cyanide is rather more soluble than zinc cyanide. Potassium tetracyanocadmate, $K_2[Cd(CN)_4]$ is readily obtained by dissolving cadmium hydroxide in aqueous potassium cyanide solution and evaporating slowly(12).

Cyanides and Cyano Complexes of the Transition Metals Table I lists some important reactions involving transition metals and cyanide ion and the equilibrium constants for these reactions(13).

Table I. Equilibrium Constants of Some Reactions Involving Transition Metals and Cyanide Ion

Reaction	Medium	Log K
$Fe^{2+} + 6CN^- \rightharpoonup [Fe(CN)_6]^{4-}$	var	24
$Fe^{3+} + 6CN^- \rightharpoonup [Fe(CN)_6]^{3-}$	O corr	31
$Co^{2+} + 6CN^- \rightharpoonup [Co(CN)_6]^{4-}$	O corr	19.09
$Co^{3+} + 6CN^- \rightharpoonup [Co(CN)_6]^{3-}$	$CaCl_2$	64
$Ni^{2+} + 4CN^- \rightharpoonup [Ni(CN)_4]^{2-}$	var	22
$[Ni(CN)_4]^{2-} + CN^- \rightharpoonup [Ni(CN)_5]^-$	O corr	-0.66
$Cu^+ + 4CN^- \rightharpoonup [Cu(CN)_4]^{3-}$	$NaClO_4$	28
$Cu^+ + 3CN^- \rightharpoonup [Cu(CN)_3]^{2-}$	var	20.78
$Cu^+ + 2CN^- \rightharpoonup [Cu(CN)_2]$	var	16
$[Cu(CN)_3]^{2-} \rightharpoonup [Cu(CN)_4]^{3-}$	O corr	1.59
$[Cu(CN)_2]^- + CN^- \rightharpoonup [Cu(CN)_3]^{2-}$	O corr	4.38
$Cu^{2+} + 4CN^- \rightharpoonup [Cu(CN)_4]^{2-}$	var	25?
$Zn^{2+} + 4CN^- \rightharpoonup [Zn(CN)_4]^{2-}$	var	16.9
$Zn^{2+} + 3CN^- \rightharpoonup [Zn(CN)_3]^-$	var	17.52
$[Zn(CN)_3]^- \rightharpoonup [Zn(CN)_4]^{2-}$	var	2.7

Table I. (continued)

$Cd^{2+} + 4CN^- \rightharpoonup [Cd(CN)_4]^{2-}$	var	18
$Cd^{2+} + 3CN^- \rightharpoonup [Cd(CN)_3]^-$	var	17.73
$Cd^{2+} + CN^- \rightharpoonup [Cd(CN)]^+$	var	5.18
$[Cd(CN)]^+ + CN^- \rightharpoonup Cd(CN)_2$	var	4.42
$Cd(CN)_2 + CN^- \rightharpoonup [Cd(CN)_3]^-$	var	4.32
$[Cd(CN)_3]^- + CN^- \rightharpoonup [Cd(CN)_4]^{2-}$	var	3.19
$Ag^+ + 2CN^- \rightharpoonup [Ag(CN)_2]^-$	var	20
$[Ag(CN)_2]^- + CN^- \rightharpoonup [Ag(CN)_3]^{2-}$	0.5 to 1.5 CN^-	0.97
$[Ag(CN)_3]^{2-} + CN^- \rightharpoonup [Ag(CN)_4]^{2-}$	0.5 to 1.5 CN^-	-0.55
$Au^+ + 2CN^- \rightharpoonup [Au(CN)_2]^-$	var	47.5
$Au^{3+} + 4CN^- \rightharpoonup [Au(CN)_4]3-$	var	56

where var represents a medium with varying ionic strength and, o corr refers to the constants that are corrected to zero ionic strength by the application of some theoretical or empirical formula.

Copper, Silver and Gold MCN, being insoluble in water, are stable. If cyanide is added to an aqueous solution of a Cu^{2+} salt, a yellow-green precipitate of copper(II) cyanide, $Cu(CN)_2$ is obtained. $Cu(CN)_2$ decomposes at room temperature with evolution of cyanogen. In an excess of cyanide the colorless $[Cu(CN)_4]^{2-}$ and $[Cu(CN)_4]^{3-}$ species are formed. $[Cu(CN)_4]^{3-}$, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ are the most stable species for Cu, Ag and Au in cyanide

solutions respectively. The ion $[M(CN)_3]^{2-}$ is an important solution species, however, for copper and silver. The overall formation constants of the $[Cu(CN)_2]^{-3}$, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ ions in aqueous solution are 10^{24}, 10^{20} and 10^{37} M^{-2} respectively(13).

Silver cyanide may be made from equivalent quantities of silver nitrate and potassium cyanide in aqueous solution. The solubility of silver cyanide in water is about $2x10^{-6}$ M at 25°C. The ions $[Ag(CN)_3]^{2-}$, $[Ag(CN)_2]^-$ and $[Ag(CN)_4]^{3-}$ are also formed in aqueous solutions(12).

Gold(I) cyanide is a yellow powder which is sparingly soluble in water, ethanol, or ether but readily soluble in aqueous cyanide solutions. The only cyano complex of gold(I) appears to be $[Au(CN)_2]^-$, the stability of which forms the basis of the cyanidation process for the extraction of gold. Cyano complexes of gold(III) such as $K[Au(CN)_4].H_2O$ and $[Au(CN)_3Cl]^-$ were also identified(14).

Iron Group The cyano complex of Fe(I) is a product of reduction of $[Fe(CN)_6]^{4-}$. Nearly all reported cyano complexes of iron(II) contain the $[Fe(CN)_6]^{4-}$ ion or its substitution product. But $[Fe_2(CN)_{10}]^{6-}$ has been shown to be present in most solutions containing Fe^{2+}:CN^- in 1:5 ratio. The best known cyano complex of iron(II), ferro cyanides (hexacyanoferrate), is made by dissolving an iron(II) salt in a hot solution of potassium cyanide and crystallizing.

Hexacyanoferrate(II) is oxidized to prussian blue or hexacyanoferrate(III) by oxygen in the presence of acid. Hot dilute sulphuric acid liberates hydrogen cyanide from hexacyanoferrates(II); the concentrated acid liberates carbon monoxide. The only well-defined iron(III) complexes containing only cyanide as a ligand are the hexacyano compounds. The $[Fe(CN)_6]^{3-}$ is rather more reactive than $[Fe(CN)_6]^{4-}$ even though it is thermodynamically more stable with respect to dissociation into the constituent ions. Since both $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ are kinetically inert species but the electron-transfer between them is very fast, the thermodynamic quantity best established in the chemistry of cyano complexes of iron is E^o:

$$Fe^{3+} + e^- = Fe^{2+} \qquad E^o=0.77V \tag{6}$$

$$[Fe(CN)_6]^{3-} + e^- = [Fe(CN)_6]^{4-} \qquad E^o=0.36V \tag{7}$$

The cyano complex of cobalt(0), $K_8[Co_2(CN)_8]$, is made by reduction of $K_3[Co(CN)_6]$ with excess potassium in liquid ammonia. Cobalt(II) cyanide is obtained as a light brownish precipitate containing 2 or 2.5 H_2O from cobalt(II) and cyanide solutions. When a solution of cobalt(II) cyanide in an excess of aqueous potassium cyanide is boiled in the presence of air cobalt (III) cyanide (hexacyanocobalate), $[Co(CN)_6]^{3-}$ is obtained. The $[Co(CN)_6]^{3-}$is very unreactive; chlorine, alkali, hydrogen peroxide, hydrochloric acid and hydrogen sulfide have no effect on it(14).

The majority of nickel cyano complexes are those of nickel(II), but there are well defined complexes of nickel(0) and nickel(I). Nickel(0) cyanide, $K_4[Ni(CN)_4]$, is prepared by reduction of $K_2[Ni(CN)_4]$ in liquid ammonia with an excess of potassium. Nickel(II) cyanide is obtained by mixing stoichiometric quantities of nickel salts and potassium cyanide in aqueous solution. Nickel(II) cyanide dissolves readily in aqueous solutions of alkali metal cyanides, the ions $[Ni(CN)_4]^{2-}$ and $[Ni(CN)_5]^{3-}$ being formed according to the $[Ni^{2+}]:[CN^-]$ ratio(15).

Cyanate and Their Thio Derivatives

The group ECN(E=O or S) is called cyanate(thiocyanate) or isocyanate(isothiocyanate) depending on whether it is bonded to the remainder of the molecule through E or through N(16). Both cyanate and thiocyanate can be formed biologically in vivo in the course of detoxication of cyanide. The reaction is mediated by an enzyme, thiosulphate sulphur transferase. Thiosulphate or even colloidal sulphur are essential cofactors. Activated carbon will catalyze the oxidation of cyanide to cyanate by dissolved oxygen. It should be pointed out that cyanate is unstable at neutral or low pH.

Organic Cyanide Species

Nitriles The most common organic cyanides are nitriles with the general formula RCN. Nitriles are sparingly soluble in water but

generally miscible in all proportions with most of the common organic solvents such as acetone, benzene, methanol, petroleum ether, and toluene. Nitriles exhibit a marked tendency to polymerize. The tendency to polymerize is the basis for the use of acrylonitrile and adiponitrile in the manufacture of acrylic or nylon fibers and synthetic rubber. Nitriles can be prepared by treatment of potassium cyanide with alkylsulfates or alkylhalides, from amides with a dehydrating agent, and by reacting aldoximes with acetic anhydride.

Isocyanides are another important category of organic cyanides with a general formula RNC. It was stated that methylisocyanide is more toxic than hydrogen cyanide, and ethylisocyanide is eightfold less so. Although known since 1686, isocyanides are little used outside the laboratory(17).

B. Methods for Cyanide Wastes Treatment

An extensive literature review is available describing mine effluent treatment techniques and cyanide removal(18). Green and Smith described various cyanide removal methods and organized these into six categories(19). Recent work by Homestake Mining Company using bacteria is included as an additional treatment method.

Natural Degradation

In this method the cyanide containing waste streams are directed to a tailing disposal area, generally a tailings pond. Environmental forces producing natural degradation include photodecomposition by sunlight, acidification by carbon dioxide in the air, oxidation by oxygen in the air, dilution, adsorption on solids, and in the case of long retention times, biological action.

Oxidation Processes

Alkaline Chlorination The use of chlorine and hypochlorite for treatment of cyanide containing waste water is the most highly developed of all the available methods from the standpoint of background experience, operating simplicity, availability of equipment and engineering expertise. The destruction of cyanide by alkaline chlorination may be accomplished by chlorine gas, calcium hypochlorite, or sodium hypochlorite(20). Major reactions involved in this process include the following:

$$NaCN + Cl_2 \rightarrow CNCl + NaCl \quad (8)$$

$$CNCl + 2NaOH \rightarrow NaOCN + NaCl + H_2O \quad (9)$$

$$2NaOCN + 3Cl_2 + 4H_2O \rightarrow 3Cl_2 + (NH_4)_2CO_3 + Na_2CO_3 \quad (10)$$

$$NaCN + NaOCl + H_2O \rightarrow CNCl + 2NaOH \quad (11)$$

All these reactions proceed to completion and are rapid; toxic metals are also removed in this process; chlorine is readily available and the process can be carried out either continuously or

in batch operation. But it also has some disadvantages: careful control of pH to prevent formation of cyanogen; chlorine is toxic; and possible formation of chlorine derivatives.

Ozonation Nearly every toxic cyanide species, hydrogen cyanide, free cyanide ions, complexes of zinc, cadmium and copper as well as thiocyanate, can be quickly destroyed by this method in which the following reactions occur(21):

$$NaCN + O_3 \rightarrow NaOCN + O_2 \quad (12)$$

$$2OCN + O_3 + H_2O \rightarrow N_2 + 2HCO_3 \quad (13)$$

$$SCN + O_3 + H_2O \rightarrow CN + H_2SO_4 \quad (14)$$

Hydrogen Peroxide The oxidation of cyanide by hydrogen peroxide can be enhanced using copper as a catalyst. The mechanism can be described by two reactions(10):

$$CN^- + H_2O_2 \rightarrow OCN^- \quad (15)$$

$$OCN^- + 2H_2O \rightarrow NH^+_4 + CO_3^{2-} \text{ (pH less than 7)} \quad (16)$$

The Inco Process In this process cyanide and metal-cyanide species are removed rapidly by oxidation of effluents with a mixture of SO_2(2.5% by volume) and air at a pH of about 9 and in the presence of a small amount of copper which acts as a catalyst. Cyanide is oxidized to cyanate, the metals, except for iron, precipitate as metal hydroxides. Iron forms insoluble ferrocyanides such as

$Ca_2[Fe(CN)_6]$ and $Zn_2[Fe(CN)_6]$. An overall reaction describing this process is(10)

$$CN_{total} + O_2 + SO_2 + H_2O \rightarrow OCN^- + H_2SO_4 \quad (17)$$

Photooxidation Heterogeneous reactions at semiconductor photocatalysts are interesting from the viewpoint of solar energy utilization. Recently, the photochemical methods for decontamination of water and industrial wastes have received a great deal of attention(22,23). Many contaminants can be completely destroyed(24,25,26) by irradiation with near UV light in the presence of photocatalysts of which titanium dioxide has been studied extensively(27,28). Mercury lamps(29), xenon lamps(30) and sunlight(31) have been used as the light source. Photodecomposition of cyanide by sunlight was noticed a long time ago. Work has been done on the photocatalytic oxidation of cyanide on titanium dioxide in both anatase and rutile forms. Results showed that both forms of titanium dioxide enhance the rate of cyanide decomposition(32). Different mechanisms of photocatalytic oxidation of cyanide have been proposed with the following being more acceptable(33):

$$(TiO_2) + 2hv \rightarrow (TiO_2)_e + 2p^+ + 2e^- \quad (18)$$

$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad (19)$$

$$CN^- + 2OH^- \rightarrow OCN^- + H_2O + 2e^- \quad (20)$$

$$(TiO_2)_e + 2p^+ + 2e^- \rightarrow (TiO_2) \quad (21)$$

Acidification/Volatilization/Reneutralization

Like the chlorination process, this method has been studied extensively(34,35). Cyanide solution is acidified and dropped through a tower counter-current to an air stream. The air which picks up the hydrogen cyanide formed by the acid from the cyanide ion and metal-cyanide complexes is swept into an absorber tower where it contacts a weak lime slurry dispersed as a mist. The absorber tower solution is recycled so as to build up usable levels of cyanide concentration for return to cyanidation processes.

Adsorption Processes

Ion Exchange A column of anion exchange resin has been used to adsorb cyanide complexes, followed by a column of the same resin to remove free cyanide(36). However, the efficiency for free cyanide adsorption is very low, and therefore, it has been proposed that free cyanide be converted to ferrocyanide by reaction with ferrous hydroxide prior to ion exchange. As one may see this process could be complicated and expensive.

Activated Carbon Activated carbon plays two roles in cyanide destruction. It both adsorbs cyanide and catalyzes the oxidation of cyanide to cyanate(37).

Ion Flotation Ion flotation used for cyanide treatment resembles

conventional froth flotation in that it employs similar equipment, and the substance to be separated is carried out of the aqueous medium as a froth of air bubbles(38). It differs in that the substance to be separated is not usually present as a solid.

Precipitation Flotation Precipitation flotation differs from ion flotation in that a colloidal precipitate is first formed and then floated(39). But in the case of cyanides, the one technique merges with the other as a result of interactions between the metals and cyanide complexes.

Electrolytic Processes

Electroreduction and Electrooxidation The reduction reaction is:

$$M(CN)_n^{-(n+2)} + 2e^- \rightarrow M + nCN^- \qquad (22)$$

where M is a divalent metal, and the oxidation reactions are

$$CN^- \rightarrow CN^0 + e^- \qquad (23)$$

$$2CN^0 + 2OH^- \rightarrow CN^- + CNO^- + H_2O \qquad (24)$$

Electrochlorination Sodium chloride is oxidized to give rise to active chlorine either at an electrode or in solution. The chlorine liberated then reacts with cyanides to form cyanates, and with thiocyanate to form cyanate and sulphate. Chloride ion is

regenerated when cyanide is chlorinated by chlorine gas and is, therefore, again available for charge transfer. Anode reaction:

$$Cl^-_{(aq)} \rightarrow Cl^0 + e^- \quad (25)$$

$$2Cl^0 \rightarrow Cl_{2(g)} \quad (26)$$

Cathode reactions:

$$H_2O + e^- \rightarrow H^0 + OH^- \quad (27)$$

$$2H^0 \rightarrow H_2 \quad (28)$$

The reactions of chlorination of cyanide are the same as those for alkaline chlorination.

Conversion to Less Toxic Forms

Conversion to Thiocyanate Cyanide is converted to thiocyanate by a mixture of peroxide and thiosulphate at pH 7 to 10(40)

$$CN^- + H_2O_2 + S_2O_3^{2-} \rightarrow SCN^- + SO_4^{2-} + H_2O \quad (29)$$

Cyanide also reacts with polysulfides to form thiocyanate(39)

$$S_x^{2-} + CN^- \rightarrow (S_{(x-1)})^{2-} + SCN^- \quad (30)$$

It is reported that at high ratios of S^{2-}/O_2, sulfide may be

oxidized to polysulfides and the conversion of cyanide to thiocyanate is, therefore, enhanced.

Conversion to Ferrocyanide Addition of excess ferrous sulphate to solutions of cyanide and the complex cyanides of zinc and copper which have been adjusted to pH between 7.5 and 10.5 converts most of the cyanide to ferrocyanide. However, This process requires close control of pH(41).

Biooxidation

Studies on biodegradation of cyanide began as early as 1945(42,43). Although large scale application of biodegradation of cyanide has not been practiced in big cyanide waste-producing industries such as mining and steelmaking industries, it is reported that free cyanide, metal complexed cyanides, and thiocyanate can be biodegraded on a laboratory scale(44,45). Allen and Strobel(46) have found that certain cyanogenic fungi are capable of assimilating hydrogen cyanide. Treatment of cyanide waste by an activated sludge process has been shown to be more efficient and less expensive than the traditional chemical processes(47,48).

Extensive pilot plant tests for biological treatment of cyanidation wastewaters have been done by the personnel at Homestake Mining Company's Homestake Gold Mine in Lead, South Dakota(49). The processes tested included activated sludge, trickling filters,

biological towers, aerated biological filters, and rotating biological contactors. Based on their studies on chemical, physical and biological processes, Mudder and Whitlock patented a biological treatment process for the degradation and removal from wastewaters of free cyanide, metal-complexed cyanides, and thiocyanates(50). According to this patent, cyanide species were oxidized to nitrates and sulfates by the microorganism strain of Pseudomonas Paucimobilis.

MATERIALS AND EQUIPMENT

Materials and Reagents

The pure minerals used for the stirred tests were obtained from the collection of specimens at the College of Mines and Minerals Science, University of Utah. Ten pure minerals were tested. They were calcite, feldspar, kaolinite, illite, rutile, quartz, hematite molybdenite, plagioclase and bauxite. The minerals were crushed and ground to -65 mesh. Table II lists the surface areas of these minerals.

Table II. Surface Areas of Minerals Used for Stirred Tests(m^2/g)

Materials	Surface Area
Quartz	0.28
Rutile	0.39
Calcite	0.67
Feldspar	0.48
Plagioclase	1.02
Illite	1.42
Bauxite	2.89
Molybdenite	3.05
Kaolinite	4.65

A soil near a mining site in Nevada was used for the tall column test. Large stones in the soil were screened out. The USDA system was used to estimate the size distribution of the soil(51), shown in Table III. The elemental composition of the soil was determined using acid digestion followed by ICP, Table IV. The finely ground soil was digested with hydrofluoric acid(48% HF), sulfuric acid(95% H_2SO_4), and perchloric acid(70% $HClO_4$) using method 1-6 from the "Methods of Soil Anaysis"(51). Important transition metals in appreciable amounts in the soil are zinc, cadmium, nickel, cobalt and iron.

Table III. Size Distribution of the Soil for the Tall Column Tests

Particle	Size Range(mm)	Per Cent(wt%)
Cobbles	**76.2-254**	**0**
Gravel	**2.0-76.2**	**30.48**
Coarse gravel	12.7-76.2	16.4
Fine gravel	2.0-12.7	14.08
Sand	**0.05-2.0**	**51.69**
Very coarse sand	1.0-2.0	5.35
Coarse sand	0.5-1.0	4.99
Medium sand	0.25-0.5	15.06
Fine sand	0.1-0.25	18.54
Very Fine Sand	0.05-2.0	7.75
Silt	**0.002-0.05**	**9.63**
Clay	**less than 0.002**	**8.19**

Table IV. Elemental Concentrations in The Soil for Tall Column Tests

Element	ppm	Element	ppm	Element	ppm
Fe	45000	Mn	830	B	780
Al	89500	Y	20	Cd	6800
Ca	29000	Li	40	As	150
K	20000	Mg	14000	Sb	3490
Na	81000	Cu	950	Te	90
V	130	Ni	2470	Sr	330
Zr	110	Co	1500	Bi	70
Cr	40	Zn	3230	P	830
Hg	510	Ba	290	Nb	20
Pb	460	W	20	Si	34150

Moisture content of the soil for the tall column tests was 9.8%. The soil has a total carbon content of 0.058% and a total sulphur content of 0.0066%. Soil pH was 7.2 analyzed using method 12-2.6.5 from the " Methods of Soil Analysis"(51).

The size distribution and elemental contents of the soil for the large tank tests are shown in Tables V and VI respectively. Copper and nickel in this soil are negligible. But, it has higher total carbon content(0.13%) than does the soil for the tall column tests.

Table V. Size Distribution of the Soil Used for Large Tanks

Particle	Size Range(mm)	Per cent
Cobble	76.2-254	0
Gravel	2.0-76.2	6
Sand	0.05-2.0	80.7
Silt	0.002-0.05	8.7
Clay	less than 0.002	4.6

Table VI. Elemental Content of the Soil for Large Tank Tests

Element	ppm	Element	ppm	Element	ppm
Fe	43700	Mn	700	B	*
Al	79200	Y	*	Ca	19000
Ca	31000	Ti	3600	As	*
K	26000	Mg	14200	Sb	*
Na	77000	Cu	*	Te	*
V	200	Ni	*	Sr	800
Zr	100	Co	*	Bi	*
Cr	*	Zn	100	P	700
Hg	*	Ba	800	Nb	*
Pb	*	W	*	Si	1500

The star in Table VI represents a concentration below the detection limit of the AA. Table VII and Table VIII show the mineral constituents of the soils determined using X-ray diffraction technique.

Table VII. Approximate Weight Percent of Mineral Components of the Soil for Tall Column Tests

Minerals	wt%	Minerals	wt%	Minerals	wt%
Quartz	34	Illite	2	Chlorite	1
K-Feldspar	15	Kaolinite	2	Gibbsite	2
Calcite	10	Hematite	6.1	Geothite	1
Plagioclase	6	Smectite	14	Other	7

Table VIII. Approximate Weight Per Cent of Mineral Components of the Soil for Large Tank Tests

Minerals	wt%	Minerals	wt%	Minerals	wt%
Quartz	9	Illite	3	Chlorite	2
K-Feldspar	21	Kaolinite	3.5	Gibbsite	5
Calcite	16	Hematite	5.6	Geothite	4
Plagioclase	18	Smectite	7	Other	6

Pure reagent grade chemicals: CuO, $ZnSO_4.H_2O$, $CdCl_2$ and $NiCl_2.6H_2O$ were used for some stirred tests. $ZnSO_4.7H_2O$ was used for making a solution containing 200 ppm Zn in the cyanide solution for large tank #2.

Equipment and Apparatus

Figure 2 shows a schematic of the apparatus used for the stirred reactor tests. The tests were conducted in a sealed, stirred one-liter glass vessel immersed in a temperature bath. Two hundred grams of pure mineral and one liter of sodium cyanide solution with a concentration of 130 ppm CN^- were added to the vessel.

The tall column is shown in Figure 3. The column has a diameter of 0.38 meters and a height of 1.82 meters. The column was filled with 80.7 kilograms of soil. A 130 ppm cyanide solution was pumped into the column at the top center at a flow rate of 0.45 mLh^{-1}. The gas phase was swept with high purity argon and sampled using a gas tight syringe for carbon dioxide, nitrogen and ammonia analyses. The void fraction of the soil in the column was 0.54 which made a pore volume of 39.63 liters.

A schematic diagram of the large tank is shown in Figure 4. The dimensions of the large tank are 1.676 meters in diameter and 0.61 meters in height. 1721 kilograms of top soil were placed into the tank. Sampling points for solution were located at different radii

and different depths. Gas samples were collected from four concentric rings that protruded into the surface of the soil about 45 mm. The void fraction of the soil was 0.43 and the pore volume was 602 liters.

Ion-chromatography, using a Dionex 400i apparatus, was used for cyanide complexes, cyanate and thiocyanate analyses. ICP, a Plasma II Emission Spectrometer made by Perkin-Elmer, was used for analyzing elemental(Fe,Co,Ni,Cu,Zn,Cd) concentrations of the effluent samples and the digestion solutions of the soils used for the tall column and large tank tests. A mass-spectrometer was used to analyze for carbon dioxide, nitrogen and ammonia in the gas samples. Surface areas of the pure minerals were determined using a BET machine, a Micrometrics model 1200 Acusorb surface area analyzer.

METHODOLOGY

A. Experimental Procedures

Stirred Test Materials tested were first put into the glass vessel. Fresh cyanide solution was then added into the reactor and the stirrer was started immediately. Pulp samples were taken from the reactor at specific time intervals and centrifuged for solid-liquid

separation. The clear solutions were analyzed for cyanate, free and total cyanide.

Tall Column Test The head space of 17.78 cm of the column was swept with argon. Before entering the column the argon was treated using KOH, heated magnesium, and H_2SO_4 absorption columns for removal of carbon dioxide, nitrogen and ammonia respectively. Then the gas phase was sampled with a gas tight syringe for N_2, CO_2 and NH_3 using mass-spectroscopy. The gas coming out from the top of the column was passed through a sodium hydroxide solution which was analyzed for HCN. Cyanide solution was pumped into the top of the column. A layer of glass wool was packed at the bottom of the column for filtering the effluent. The filtered effluent came out through a plastic tube and was collected in an Erlenmeyer flask. The pH, cyanide species and elemental concentrations of the effluent were measured.

After the solution pumping was stopped and the effluent stopped dripping from the tube the soil column was cut into four sections. Solid samples were taken from each section. Each solid sample was divided into six portions. One portion was analyzed for free and total cyanide directly using the distillation-colorimetric method. Other portions were washed with distilled water and solutions of different pH values. The wash solutions were analyzed for CN^-, OCN^-, SCN^- and cyanide complexes.

Large Tank Tests Fresh cyanide solution was pumped into the top center of the tank. Twenty eight sampling points for solution were located at different radii from the center of the tank, 10.16, 30.48, 50.8 and 71.12 cm. These sampling points were also located at different depths from the bottom of the tank, 38.1, 25.4 and 12.7 cm. A plastic funnel filled with glass balls was placed at each sampling point for filtering and collecting the effluent. The tank was covered with a baffled cover so that the head space of the tank was divided into four baffled rings with a average radius of 10.16, 30.48, 50.8 and 83.82 cm. The gas phase in each ring was swept with nitrogen and passed through a sodium hydroxide solution for HCN analysis.

B. Analytical

Electrode Method for Cyanate An ammonia electrode was used for most of the cyanate analyses(52). The sample solution(100 mL) was first heated at low pH, approximately 2, at 90 to 95° C for 30 minutes so that the cyanate hydrolyzes to ammonia according to reaction (31)

$$2NaCNO + H_2SO_4 + 4H_2O \rightarrow (NH_4)_2SO_4 + 2NaHCO_3 \qquad (31)$$

The sample was then cooled to room temperature and restored to its original volume by adding ammonia-free water. The sample was poured into a 250-mL beaker and stirred with a magnetic stirrer. The electrode was immersed into the beaker. One milliliter of 10N NaOH

solution was added into the sample to adjust the pH to 11 or above. After equilibrium had been reached, the potential reading from an Eh meter was recorded and the ammonia content was determined from calibration curve(52).

Distillation-Colorimetric Method for Free and Total Cyanide A portion of sample was added into a one-liter distillation flask. For weak acid dissociable cyanide, acetate buffer, zinc acetate and water were added. Twenty mL of NaOH solution was poured into a gas absorber with some $PbCO_3$ to precipitate S^{2-}. The sample was boiled for about one hour. CN^- was liberated as HCN and absorbed in the sodium hydroxide solution for analysis. For total cyanide 50mL of H_2SO_4(1:1 solution), instead of acetate buffer, was poured into the flask. $MgCl_2$ and $HgCl_2$ were added into the flask for catalyzing the dissociation of the iron and cobalt cyanide complexes.

CN^- in the alkaline distillate from the previous treatment is converted to CNCl by the reaction with chloramine-T at a pH less than 8, which is achieved by adding acetate buffer. After the reaction is complete, CNCl forms a red-blue dye on addition of pyridine-barbituric acid reagent. If the dye is kept in an aqueous solution, the absorbance is read at 578nm. To obtain colors of comparable intensity the salt content in the sample and the standards were maintained the same(53).

Titrimetric Method for Free Cyanide For some clear samples with

high concentrations of cyanide(more than 5mg CN^-/L) a quick and simple titrimetric method was used for free cyanide analysis. CN^- in alkaline solution is titrated with standard silver nitrate with 1mL of $AgNO_3$ solution being equal to 1mg CN^-. Cyanide reacts with silver nitrate to form the soluble cyanide complex, $[Ag(CN)_2]^-$. As soon as all of the CN^- has been complexed and a small excess of Ag^+ has been added, the excess Ag^+ is detected by the silver-sensitive indicator, P-dimethylamino-benzalrhodanine, which immediately turns from a yellow to a salmon color. A measured volume of sample was diluted to 250 mL using the NaOH dilute solution and titrated with standard $AgNO_3$ titrant to the first change in color from yellow to salmon. A blank containing the same amount of alkali and water was also titrated. The concentration of cyanide is finally calculated by the following formula:

$$mgCN^-/L=2500(A-B)/(mL\ original\ sample).(mL\ portion\ used)$$

where: A=mL standard $AgNO_3$ for sample and

B=mL standard $AgNO_3$ for blank

ICP for Metal Elements Concentration Atomic emission spectroscopy, (AES) atomic absorption spectroscopy(AAS) and atomic fluorescence spectrocopy(AFS) are three branches of analytical spectroscopy which derive analytical information from atomic spectra in the optical region of the electromagnetic spectra. In all three methods the sample must be atomized. Combustion flames provide a remarkably

simple means for converting inorganic analytes in solution into free atoms. Once the free atoms are formed they may be detected and determined quantitatively at trace levels by the above three methods. Electrically generated "flames", plasma, possess higher gas temperatures and less active chemical environments. Inductively coupled plasma, ICP, are chiefly used as excitation sources for AES(54,55).

The PERKIN-ELMER Plasma II Emission Spectrometer system was used for most of the metal elements analyses. Figure 5 shows the components and the schematic arrangement of the system. This system has seven major components: Plasma II spectrometer, Plasma II torch, PE 7500 computer, PR-210 printer/plotter, AS-51 autosampler, RF power supply and vacuum pump. Samples can be analyzed using standard conditions or using element parameters selected by the analyst. The standard conditions method was used in this study.

Plasma is generated in the torch which is set up in a water-cooled coil of an rf generator. The torch consists of three tubes: an outer tube, an intermediate tube and an inner tube. Flowing gas is introduced into the torch, the rf field is switched on the gas in the coil and is made electrically conductive by Tesla sparks. Then a plasma will be formed, provided the magnetic field strength is high enough and the gas streams follow a particular, rotationally symmetrical pattern. This inductively coupled plasma thus formed is maintained by inductive heating of the flowing gas in a way similar

to the inductive heating of a metallic cylinder placed in the induction coil, that is, the rf currents flowing in the coil generate oscillating magnetic fields with lines of force axially oriented inside the coil. These magnetic fields generate in turn high frequency, annular electric currents in the conductor, which is then heated as a result of its ohmic resistance.

Operation of the Plasma II spectrometer is completely controlled by the system software. The Plasma II Applications software is organized into several major operating modes. These include parameter entry modes, directory modes, an analytical mode, a support mode and a report mode.

Ion-Chromatography for Anionic Cyanide Species

Ion chromatography is an analytical technique utilizing multiple modes of separation and multiple modes of detection to provide for the routine quantitation of ionic species in the sub ug/L(sub ppb) to mg/L(ppm) range. Three different modes of separation are currently employed:

Mobile Phase Ion Chromatography(MPIC)
High Performance Ion Chromatography(HPIC)
High Performance Ion Chromatography Exclusion(HPICE)

The three modes are characterized by the types of polystyrene or divinylbenzene resin shown in Table IX.

Table IX. Characteristics of the Resins for the Three Modes of Separation for Ion Chromatography(56)

Types of Resins for Analysis	Ion Exchange Capacity
HPIC-modestely low, fixed ion exchange capacity	0.01-0.05meq/g
MPIC-no fixed ion exchange capacity	0
HPICE-high fixed ion exchange capacity	3-4 meq/g

There are a variety of detection modes employed in modern IC, they are summarized in Table X.

Table X. Ion Chromatography Detection Modes and Their Principle and Application in Anion Analysis(56)

Detection Mode	Principle	Use
Ion Chro/Cond	Conductivity	Ions that significantly inoize in solution
Ion Chro/Amp and Ion Chro/pulsed Amp	Amperametry and Pulsed Amperametry	Ions which can be oxidized or reduced: Cl^-, Br^-, I^-, S^{2-}, CN^-, SO_3^{2-}, $S_2O_3^{2-}$, OCl^-, Alcohols, Carbohydrates, Phenols, Amines, hydrazine
Opti ion/UV-Vis	Light Adsorption	S^{2-}, SO_3^{2-}, SCN^-, $S_2O_3^{2-}$, $NO_2^-N_3^-$, Br^-, I^-, $IO_3IO_2^-$, $Se_2O_3^{2-}$, $Se_2O_4^{2-}$, $SeCN^-$, AsO_3^{3-}, AsO_4^{3-}
Opti Ion/Flour	Fluorescence	Aromatics, Amino acids

In this study, a Dionex Model 4000i ion chromatograph was used with a Dionex(Opti Ion/UV-Vis) spectrophotometric detector and a Dionex 4270 integrator. The Mobile phase ion chromatography(MPIC) technique was used for analyses of anionic cyanide in solution samples. This technique utilizes a hydrophobic column packing, a hydrophilic mobile phase containing an ion pairing reagent, and a

suppressor to lower the mobile phase background conductivity before entering a conductivity detector. Figure 6 is a schematic diagram of the IC. In order to successfully determine any species by MPIC the analyte must satisfy three criteria: (a) be soluble in a mobile phase consisting primarily of H_2O, H_2O/CH_3CN or H_2O/CH_3OH, (b) be an anion or cation in order to ion pair with the pairing reagent in the mobile phase and (c) be detectable via conductivity, UV or electrochemistry. Samples were centrifuged prior to injection onto the column so that they were completely in solution and free of particulates before injection.

Nitrate and Nitrite in Solution and Soils Concentrations of nitrate and nitrite in solution samples were analyzed directly using ion chromatography. For nitrate and nitrite in soils, 25 grams of soil were placed in a 250-mL flask, 100 mL of dilute sodium hydroxide solution at the same pH as the fresh cyanide solutions for the column(pH=10.5) and tank(pH=12.5) test was added. The flask was stoppered and shook on a mechanical shaker for approximately one hour. The soil-solution suspension was then filtered. Nitrate and nitrite analyses were performed on the filtrate by ion chromatography.

Mineralogical Aynalysis Approximate mineral constituents of the soils were analyzed using X-ray diffraction technology. Before it was analyzed by X-ray diffraction, the soil sample was pretreated in several steps. The first step is removal of soluble salts and

carbonates by dissolving the sample in sodium acetate buffer. In the second step organic matter was removed by oxidizing with hydrogen peroxide. Finally free iron oxides, mostly hematite, were extracted by sodium dithionite and saturated sodium chloride solution. The pretreated soil sample was then ground to a fine powder using a small ceramic ball mill. Powder samples were mounted into a rod for random orientation and the x-ray diffraction patterns were quantitatively analyzed.

RESULTS

Stirred Tests with Pure Minerals

Most of the stirred tests were run for 24 hours. At least five samples were taken for each test. The fraction of free cyanide reacted was plotted versus time. Figure 7 shows the first-order plots of cyanide attenuation in pure minerals which attenuate cyanide appreciably. Table XI lists the data. Figure 8 shows plots for those minerals that do not attenuate much cyanide, (Table XII). Kaolinite degrades cyanide the most and hematite the least.

The final solution and the solids of all the stirred tests were analyzed for free cyanide, cyanide complexes and cyanate for mass

balance analysis on CN^-. Since the reactor was sealed and the final pH of the solutions was about 10, volatilization of cyanide as hydrogen cyanide was negligible. Table XIII lists the distribution of cyanide losses through the different mechanisms for several minerals.

Table XI. Data for Stirred Tests for Reactive Pure Minerals With Time Versus $[1-C/C_o]$ for Free Cyanide

Time(hrs)	Feldspar	Plagioclase	Bauxite	Molybdenite	Kaolinite
0.00	0.000	0.000	0.000	0.000	0.000
2.60	0.014	0.021	0.027	0.034	0.040
7.90	0.051	0.060	0.075	0.088	0.098
14	0.087	0.096	0.122	0.142	0.154
19.30	0.118	0.125	0.155	0.178	0.190
24	0.143	0.153	0.184	0.200	0.230

Table XII. Data For Stirred Tests for Unreactive Pure Minerals with Time versus $[1-C/C^{o}]$ for Free Cyanide

Time(hrs)	Quartz	Calcite	Rutile	Illite	Hematite
0.00	0.000	0.000	0.000	0.000	0
2.00	0.002	0.003	0.006	0.008	0
6.86	0.003	0.004	0.013	0.015	0
12.00	0.005	0.008	0.024	0.026	0
17.14	0.007	0.010	0.030	0.033	0
24	0.010	0.016	0.040	0.044	0

Table XIII. Cyanide Distribution for Pure Minerals

Minerals	CN^- Loss	CN^- Complexed	CN^- Oxidized	CN^- Adsorbed
Feldspar	14.3%	1.3%	1.02%	11.4%
Plagioclase	15.3%	1.43%	1.00%	13.11%
Bauxite	18.4%	3.25%	4.06%	10.22%
Molybdenite	20%	2.13%	3.04%	13.34%
Kaolinite	23.1%	0.9%	1.11%	19.87%

Tall Column Test Results

The tall column ran for 335 days with 361.11 liters of cyanide solution being pumped into the column. Because the flow rate of solution was small, about 45 $mLhr^{-1}$, the soil was initially unsaturated. Table XIX lists the major data for the tall column test. Instead of using a time scale, the rate of free cyanide disappearance and the formation of other cyanide species as well as elemental concentrations in the effluent are plotted against pore volumes of cyanide solution pumped into the column.

Figure 9 indicates free and total cyanide change in the effluent as a function of pore volume. Compared to the initial concentration of cyanide in the fresh solution, both free and total cyanide concentrations in the effluent are negligible, 46.93 grams of cyanide was added into the column but only 0.573 grams of cyanide were detected in the effluent, which indicates that 98.78 per cent of the cyanide added was degraded or adsorbed.

Figure 10 shows concentration of cyanate versus pore volume for the tall column. Cyanate was only found in the early stages of the test. After 1.33 pore volumes of cyanide solution were added(50 days after the start) no cyanate was detected in the effluent. Thiocyanate was not found in any samples of the test.

To determine how much cyanide was volatilized as hydrogen cyanide, the cumulative HCN collected from the gas phase was divided by total cyanide added to obtain a percentage of cyanide

volatilized. The percent of HCN was then plotted versus pore volume, Figure 11. At 2.10 pore volumes a maximum volatilization of 4.48% was reached. As the soil approached saturation volatilization decreased.

Figure 12 is a plot of pH of the effluents versus pore volume. The pH of the fresh cyanide solution was 10.5, which dropped to 8 or below when the solution exited the column. Although the values of pH of the effluent fluctuated incessantly they fit a second-order polynomial quite well; the correlation equation is

$$pH=8.50 - 0.488PV + 4.911\times10^{-2}(PV)^2 \qquad (i)$$

Where PV represents the pore volume. The pH decreased initially to a minimum value of 7.3 and then increased as more fresh cyanide solution was added. Figure 13 is a plot of cobalt concentration in the effluent of the tall column versus pore volume. Although appreciable amounts of iron, zinc and cadmium exist in the soil, only nickel, cobalt and copper were found in the effluent. The fact that no Fe, Zn or Cd were found in solution raised the question that these metals might be complexed with cyanide and precipitated in the soil. Figure 14 shows concentrations of nickel, copper and cobalt in the column effluent versus pore volume. From this figure it is seen that Ni, Co and Cu were leached out by cyanide from the soil sequentially with Ni being the first, followed by Co and finally Cu.

Figure 15 shows concentrations of cyanate, nickel and copper versus pore volume. The maximum concentration of cyanate appeared near the concentration peaks of both nickel and copper. Cyanate concentration dropped to zero as these metal elements in the effluent depleted.

Some typical ion-chromatographic plots of the column effluent are shown in Figures 22(a) to 22(c). There are four major peaks, all of which are identified: free cyanide, nitrate, copper-cyanide complex and nickel-cyanide complex. A quantitative calculation for nickel, cobalt and copper cyanide complexes was done, in which the measured concentrations of $[Ni(CN)_4]^{2-}$, $[Co(CN)_4]^{3-}$ and $[Cu(CN)_4]^{3-}$ were compared with calculated concentrations based on elemental concentrations of Ni, Co and Cu from ICP data, Table XIV.

Table XIV. Comparison Between the Calculated and Measured Concentrations of Metallo-Cyanide Complexes in the Column Effluents

Element Concentration by ICP	Complex Measured Using Ion Chromatography	Potential Complex Formations Calculated from ICP Data
Cu(ppm)	**$[Cu(CN)_4]^{3-}$(ppm)**	**$[Cu(CN)_4]^{3-}$(ppm)**
0.34	0.79	0.896
0.52	1.06	1.37
1.28	3.05	3.37
Ni(ppm)	**$[Ni(CN)_4]^{2-}$(ppm)**	**$[Ni(CN)_4]^{2-}$(ppm)**
1.39	3.61	3.85
2.90	8.19	8.04
3.34	10.10	9.26
Co(ppm)	**$[Co(CN)_6]^{4-}$(ppm)**	**$[Co(CN)_6]^{4-}$(ppm)**
0.87	3.10	3.17
1.23	4.05	4.49
1.54	5.23	5.62

The samples in Table XIV were randomly selected from the tall column effluents. The pore volumes of cyanide solution added corresponding to these samples are 0.665, 0.910, 0.740, 0.614, 0.779, 0.896, 0.926, 0.853, and 0.798 from the top to the bottom in Table XIV. The first column of Table XIV lists Cu, Ni and Co concentrations in the column effluents using ICP. The second column shows the corresponding concentrations of metal cyanides measured using ion chromatography. The data in the third column are calculated based on ICP data in the first column.

In order to find out how much and under what conditions metallo-cyanides precipitate in soil, solid samples were washed with distilled water, acidic solutions and basic solutions. Table XV shows how the concentrations of metllo-cyanides in the wash solutions change with pH.

Table XV. Effect of pH on Concentrations of Metallo- Cyanide Precipitates in the Wash Solution Filtrate for the Tall Column Soil(ppm)

pH	$Zn(CN)_2$	$Ni(CN)_2$	$Cd(CN)_2$
7	0	0	0.21
9	0	0	0.67
9.5	0.13	0.08	1.01
10	0.98	0.62	1.32
10.5	1.23	0.79	1.48
11	1.31	0.86	1.66
11.5	1.77	1.01	1.79
12	1.79	1.03	1.82
13	1.79	1.03	1.83

The data in Table XV were obtained in several steps. First, 50 grams of solid from the tall column was mixed and washed with 250 milliliters of solution of specific pH for eight hours and the mixture was filtrated. Then, the filtrate was analyzed for Zn, Ni and Cd concentrations using ICP. Finally, concentrations of metal cyanides were calculated based upon the corresponding metal concentration. It may be seen from Table XV that in the pH range

from 11.5 to 13 the metal cyanide concentrations change very little and, therefore, the concentration at pH 13 should represent the maximum amount of metal cyanide precipitated on the soil. Calculations based on the data at pH 13 indicate that more than 12 per cent of cyanide added was precipitated as metallo- cyanide compounds. Table XV also shows that $Zn(CN)_2$ and $Ni(CN)_2$ precipitate at a pH as high as 9, and $Cd(CN)_2$ can only precipitate at pHs below 7. Figures 34 through Figure 36 show the effect of pH on the concentrations of $[Zn(CN)_4]^{2-}$, $[Ni(CN)_4]^{2-}$, and $[Cd(CN)_4]^{2-}$ in the wash solutions of the final solid for the tall column test.

The amount of free cyanide adsorbed on the soil was analyzed using the distillation-colorimetric method. Free cyanide concentration in the solids averages 67.91 ppm which gives 11.7 per cent of cyanide adsorption on soil.

Concentrations of nitrate and nitrite in both soils and solution samples were analyzed using ion chromatography. Figure 41 indicates the rates of cyanide transformation to nitrate for the tall column. A little nitrite was found in a few solution samples for the tall column and tank #2 tests. No nitrite was detected in the soils of both tests. Nitrate concentration in the soil for the tall column test is found to be 28.4 ppm.

Large Tank Test Results

Figures 23-26 are plots of accumulated percent of hydrogen cyanide versus time in the four concentric rings for tank #1. An average radius was used for each ring. Except for the first ring, hydrogen cyanide volatilization from each ring is a parabolic function of time. Figure 27 is a plot of total hydrogen cyanide collected from all four rings versus time. Figures 28 through 32 are corresponding figures for tank #2. Slightly more HCN was collected from tank #2 than tank #1, which may be attributed to the higher cyanide concentration of the solution used for tank #2. Figure 33 compares the two tanks for total hydrogen cyanide volatilized. Table XX lists some data for the large tank tests.

Concentrations of nitrate and nitrite in both soils and solution samples were analyzed using ion chromatography. Figure 42 indicates the rate of cyanide transformation to nitrate for large tank #2 test. The nitrate concentration in the soil for the large tank test is 103.6 ppm.

The advancement of the wet front for the large tanks were recorded Daily, Table XXII, and ploted in Figures 43 and 44.

Stirred Tests with Reagent Grade Chemicals

The reactions of CuO and $NiCl_2.6H_2O$ with cyanide were studied using the stirred reactor. Solution samples were analyzed for free cyanide and cyanate. Free cyanide decreased by 90% within 20 hours.

Figure 16 compares the rate of cyanate formation in a copper containing cyanide solution to that in a nickel containing cyanide solution in a stirred reactor. Figure 17 shows plots of the logarithm of cyanate concentration versus time for Cu and Ni containing cyanide solution in a stirred reactor. Figure 18 shows the change of free cyanide with time and Figure 19 is a plot of cyanate concentration versus time for the CuO containing cyanide solution. Cyanate accounts for 9.65 percent of free cyanide lost. The rest of the cyanide was complexed with copper. Figures 20 and 21 are corresponding figures for $NiCl_2.6H_2O$ containing cyanide solutions. The amount of cyanate formed is slightly less with nickel chloride than with copper oxide.

Figures 37-40 indicate the effect of pH on precipitation of $Zn(CN)_{2(s)}$, $Cd(CN)_{2(s)}$, $Cu(CN)_{(s)}$ and $Ni(CN)_{2(s)}$ in cyanide complex solutions of Zn, Cd, Cu and Ni, respectively. The zinc cyanide solution was made by the reaction of cyanide with zinc sulphate in aqueous solution containing 200 ppm zinc; cadmium cyanide solution was made by reaction of cyanide with cadmium chloride containing 200 ppm cadmium; copper cyanide solution was made by reaction of cyanide with cupric oxide; and nickel cyanide solution was made by reaction of cyanide with nickel chloride. Data corresponding to Figures 37 to 40 are shown in Table XVI.

Table XVI. Effect of pH on Precipitation of Metallo-cyanide Complexes in Reagent Grade Chemical Solutions(ppm)

pH	$Zn(CN)_2$	$Cd(CN)_2$	$Cu(CN)$	$Ni(CN)_2$
1	*	*	52	0.110
2	*	*	52	0.080
3	5	*	48	0.045
3.5	60	2	12	0.022
4	90	5	8	0.002
4.5	93	13	5	*
5	95	43	*	*
5.5	100		*	*
5.67		60	*	*
6	95	52	*	*
6.5	60	25	*	*
7	20	15	*	*
7.5	10	8	*	*
8	5	*	*	*
9	3	*	*	*
10	*	*	*	*
11	*	*	*	*

The star represents a concentration below the detection limit, 0.01 ppm, of the equipment. The concentrations in Table XVIII were obtained by the following steps: (1) One liter of 130 ppm cyanide solution with 200 ppm metal was added into the reactor. Sulfuric acid or concentrated sodium hydroxide solution was added to adjust the pH of the solution. The solutions were then stirred for four hours, long enough for the system to reach equilibrium; (2) The reaction products were filtered. The precipitate was washed with 100 mL of pH 13 NaOH solution; (3) The concentrations of the metal in the wash solution was measured, and the concentration of metal cyanides based on the original volumes of solutions were calculated stoichiometrically.

DISCUSSION

Reaction of Cyanide With Pure Minerals

Ten mineral components of soil were tested and five of them are found to attenuate cyanide in stirred reactor tests in appreciable amounts ranging from twelve to twenty three per cent of the cyanide originally added within twenty four hours. The promising minerals are K-feldspar, kaolinite, plagioclase, molybdenite and bauxite. Hematite, quartz, calcite, rutile and illite are found to attenuate little cyanide, less than 4 per cent in 24 hours. Since

the reactor was sealed and the final pH of the solutions was approximately 10, volatilization of cyanide as hydrogen cyanide was negligible. No cyanate was found in the final solutions either. Most of the cyanide lost in solution was adsorbed on the solids. If adsorption is the major mechanism for pure minerals to attenuate cyanide, the rates of cyanide disappearance in solution should be first-order. In fact, the experimental data correlate well with a first-order equation, Figures 7 and 8. The data for the promising minerals were treated using the least square method and they all fit first-order equations with a correlation coefficient of 0.994 or better, Table XVII.

Table XVII. First-Order Fit of the Data for Pure Minerals. k is the Reaction Rate Constant and R the Correlation Coefficient

Minerals	k (min^{-})	R
K-Feldspar	0.00646	0.9997
Plagioclase	0.00683	0.9992
Bauxite	0.00843	0.9983
Molybdenite	0.00939	0.9941
Kaolinite	0.0106	0.9974

Recalling that the surface area increases from feldspar to kaolinite, we see that the value of the adsorption rate constant

increases with increasing surface area, indicating that reaction of cyanide with these minerals is a surface controlled adsorption process. Another important observation is that all the minerals, except for molybdenite, which adsorb cyanide have a high content of alumina, and that kaolinite, highest in alumina, attenuates cyanide the most. While the minerals with high content of calcium and silicon do not tend to adsorb cyanide.

Mechanisms of Cyanide Attenuation in Soils

Volatilization The pH of the cyanide waste effluent in most cyanidation operations is ten or above. Soil pHs are usually close to 7. When cyanide solution contacts soil either through solution leaks or intentionally the pH of the solution will drop to eight or less, at which point more than 90 per cent of cyanide exists as hydrogen cyanide. If there were no other reactions occuring nearly all of the cyanide would be eventually volatilized. But that is not the case. Soil is such a complex material that cyanide reacts with it in many different ways.

The extent and rate of volatilization of cyanide as hydrogen cyanide in soil depend on many factors, such as pH, surface area available for volatilization, hydraulic conductivity and porosity of the soil, temperature, concentration and extent of saturation of

the soil. This study suggests that the most important parameters which affect the volatilization are pH, porosity and surface area. If volatilization accounts for less than 15 per cent under the conditions of large tank and unsaturation it is not the major mechanism for cyanide attenuation in soils.

Oxidation Because of their relative instability and low toxicity, inorganic cyanates pose few environmental problems. It is found that sodium and potassium cyanates, when compared to cyanide are relatively nontoxic to humans and animals(57). Oxidation of cyanide to cyanate has generated a great deal of interest in the area of waste treatment, particularly, for cyanide-containing waste water.

Cyanide may be oxidized by the following reagents: chlorine or hypochlorite(20); photocatalytically by oxygen(22,23,25); ozone(21); a mixture of oxygen and sulphur dioxide(10); MnO_2 or $K(MnO_4)$(17); peroxide(18); heat or by microorganisms(12).

Oxidation of cyanide in aqueous solution by oxygen is thermodynamically possible through reaction (32)

$$2CN^- + O_2 \rightarrow 2OCN^- \qquad (32)$$

Cyanate formed may be hydrolyzed to carbon dioxide and ammonia under appropriate conditions(reaction 33)

$$OCN^- + 2H_3O^+ \rightarrow CO_2 + NH_4^+ + H_2O \qquad (33)$$

However, reaction (32) is impractically slow, if not impossible, under normal conditions. Efforts have been made in a search for catalysts which enhance the oxidation of cyanide by dissolved oxygen. It was found that cyanide adsorbed on activated carbon can be catalytically oxidized to cyanate(58,37,59). Hoecker and Muir(59), and Bernardin(37) have shown that the presence of copper accelerates the catalytic oxidation of cyanide by oxygen on activated carbon. Copper was also used as a catalyst in the SO_2/Air oxidation process for cyanide-containing wastewater(60).

Among the potential catalysts, copper has been studied relatively extensively. However, the mechanism of this catalysis has not been appropriately addressed. It was also not convincingly proved whether it is the cationic copper(Cu^{2+}) or the metallo-cyanide complex($[Cu(CN)_4]^{3-}$) that catalyzes the oxidation of cyanide. Since the complexation of cyanide ion by copper is a very fast reaction and oxidation of cyanide is much slower, the oxidation may actually be catalyzed by the $[Cu(CN)_4]^{3-}$ complex. It was the intention of this study to identify the catalytic effect of copper and nickel on the oxidation of cyanide to cyanate.

Reagent grade CuO and $NiCl_2.6H_2O$ were used for the stirred tests. A 100 ppm Cu solution was made by adding 0.125g CuO to one liter of cyanide solution containing 200 ppm CN^-, and a 100 ppm Ni

solution was made by adding 0.4047g $NiCl_2.6H_2O$ to one liter of cyanide solution containing 200 ppm CN^-.

(1) Oxidation of Cyanide in Soils

As previously noted, cyanide can be oxidized by many oxidants. Though none of these oxidants are known to be present in the column, appreciable amounts of cyanide were oxidized to cyanate. Figure 15 is a plot of cyanate, Cu and Ni concentrations versus pore volume. Oxidation occurred initially and was fast. After 1.3 pore volumes of cyanide solution was added the oxidation stopped. Mass balance calculations indicated that approximately four percent of the cyanide added was oxidized to cyanate.

The concentrations of both nickel and copper decreased to near zero after about 1.3 pore volumes of cyanide solution were pumped into the column, and the maximum concentrations of cyanate, nickel and copper all exit the column at approximately the same time. These facts suggest that oxidation of cyanide to cyanate may be linked to the leaching of nickel and copper from the soil. The question that remains is whether Cu^{2+} and Ni^{2+}, or the metallo-cyanide complexes, $[Cu(CN)_4]^{3-}$ and $[Ni(CN)_4]^{2-}$, play the role of catalysts.

Elemental concentrations of nickel and copper in the effluent were analyzed as a function of pore volumes. Assuming that copper com-

plexes with cyanide to form $[Cu(CN)_4]^{3-}$, and with nickel to form $[Ni(CN)_4]^{2-}$, we found that the calculated concentrations of the metallo-cyanide complexes based on ICP data are quite consistent with the corresponding measured concentrations using ion chromatography(Table XVII). The stoichiometric factor is 2.6366 for copper and 2.7714 for nickel.

The pore volumes of cyanide solution added corresponding to the samples in the first column of Table XIV were 0.665, 0.910, 0.741, 0.614, 0.779, and 0.896 from the top to the bottom.

Since the complexation of nickel and copper with cyanide is fast and complete it is reasonable to suggest that the metallo-cyanide complexes, instead of the metallic cations, have the catalytic effect on the oxidation of cyanide to cyanate.

(2) Oxidation of Cyanide in CuO and $NiCl_2.6H_2O$

In an effort to confirm the above hypothesis stirred batch reactor tests were conducted using reagent grade CuO and $NiCl_2.6H_2O$. Figures 19 and 21 show that oxidation of cyanide does indeed occur in both copper and nickel containing solutions.

The rates of reactions of cyanide with CuO and $NiCl_2.6H_2O$, as shown in Figures 18 and 20, can be divided into two distinct stages. In the first stage, from the beginning to about 250 minutes, rapid

complexation of cyanide with the metal was accompanied by slow oxidation of cyanide to cyanate. In the second stage oxidation of cyanide to cyanate took over exclusively with a much slower pseudo-first order rate. Calculations indicate that cyanate formed in the second stage accounts for more than ninety per cent of the cyanide lost in this stage, Table XVIII, suggesting that large amounts of oxidation of cyanide occurred only after most of the copper in CuO, or the nickel in $NiCl_2.6H_2O$ was complexed with cyanide. Therefore, the oxidation process was catalyzed by the metallo-cyanide complexes formed, not the metal cations.

Table XVIII. Comparison of Free Cyanide lost in the Second Stage to Cyanide Oxidized to Cyanate for CuO and $NiCl_2.6H_2O$

Chemical	CN^- lost(ppm)	CN^- oxidized to OCN^-(ppm)
CuO	14.3	12.55
$NiCl_2.6H_2O$	12.9	11.76

Results indicated that cyano cuprates and cyano nickelates have similar catalytic activities for cyanide oxidation. Figure 16 compares the rate of cyanate formation in cyanide solution

containing 200 ppm copper with that containing 200 ppm nickel. Plotting the logarithm of cyanate concentration versus time, Figure 17, we found that the rate constants for copper and nickel are about the same, 0.004 versus 0.0047.

Three control tests were conducted in the absence of copper and nickel. Test one was run using one liter of cyanide solution containing 200 pm CN^-. The solution was stirred for 24 hours. In test two, oxygen was bubbled through the cyanide solution with agitation for 24 hours. Test three used one liter of cyanide solution with 100 ppm cobalt added as cobalt sulfate, $CoSO_4.7H_2O$. In all three tests the cyanate concentration in the final solution was negligible.

(3) Mechanisms of the Catalytic Oxidation

(i) Heterogeneous Mechanism In the soil the catalytic oxidation may occur both homogeneously and/or heterogeneously. Studies have shown that activated carbon and organic carbon have a high capacity of adsorbing oxygen and, therefore, catalyze the oxidation of cyanide adsorbed on the carbon to cyanate.(58,42,61-63). It is also verified that metallo-cyanide complexes, particularly copper and nickel, adsorb more extensively than either CN^- or the metallic cations(58,37).

Activated carbon and organic carbon both exist in soils. Therefore,

nickel and copper may actually act as a CN^- carrier via their complexation with CN^- and the readiness of adsorption of their complexes. Copper and nickel which has been previously adsorbed by the carbon are released into solution once the cyanide ions complexed with them are oxidized. The released copper and nickel again complex with cyanide, adsorb on the carbon, and the complexed cyanide is again oxidized. Thus, the heterogeneous catalytic process consists of the following steps:

Complexation of metallic ions with CN^-:

$$2Cu^{2+} + 10CN^- \rightleftharpoons (CN)_2 + 2[Cu(CN)_4]^{3-} \quad (34)$$

$$Cu^+ + 4CN^- \rightleftharpoons [Cu(CN)_4]^{3-} \quad (35)$$

$$Ni^{2+} + 4CN^- \rightleftharpoons [Ni(CN)_4]^{2-} \quad (36)$$

Adsorption of oxygen and complexes on carbon:

$$[Cu(CN)_4]^{3-}_{(aq)} \rightarrow [Cu(CN)_4]^{3-}_{(adsorbed)} \quad (37)$$

$$[Ni(CN)_4]^{2-}_{(aq)} \rightarrow [Ni(CN)_4]^{2-}_{(adsorbed)} \quad (38)$$

$$O_{2(dissolved)} \rightarrow O_{2(adsorbed)} \quad (39)$$

Oxidation of CN^-:

$$[Cu(CN)_4]^{3-}_{(ad)} + 2O_{2(ad)} \rightarrow Cu^+_{(ad)} + 4OCN^-_{(ad)} \quad (40)$$

$$[Ni(CN)_4]^{2-}_{(ad)} + 2O_{2(ad)} \rightarrow Ni^{2+}_{(ad)} + 4OCN^-_{(ad)} \quad (41)$$

Desorption of the oxidation products:

$$Cu^{+}_{(ad)} \rightarrow Cu^{+}_{(aq)} \quad (42)$$

$$Ni^{2+}_{(ad)} \rightarrow Ni^{2+}_{(aq)} \quad (43)$$

$$OCN^{-}_{(ad)} \rightarrow OCN^{-}_{(aq)} \quad (44)$$

(ii) Homogeneous Mechanism In the case of homogeneous catalytic oxidation the metal ions commonly cycle between two relatively stable oxidation states. The most important characteristics of metal catalysis for affecting oxidation are the accessibility of several oxidation states as well as the accommodation of various coordination numbers, both of which are properties of transition metal complexes(64-66).

The rate of oxidation with copper and nickel complexes, unlike the metal ion-catalyzed oxidation reactions, has been found to be independent of oxygen concentration(67). This suggests that the rate-determining step is a one-electron reduction of the complex species by an initiator followed by a fast reoxidation of the low valent metal complex by molecular oxygen.

Based on the above discussion and some indications in this study the following mechanism is proposed for the homogeneous catalysis:

Formation of high valence compounds:

$$2Cu^{2+} + 10CN^- \rightarrow (CN)_2 + 2[Cu(CN)_4]^{3-} \quad (45)$$

$$[Cu(CN)_4]^{3-} + 2O_2 \rightarrow 4OCN^- + Cu^+ \quad (46)$$

$$Cu^+ + 2OH^- \rightarrow CuO + H_2O + e^- \quad (47)$$

$$Ni^{2+} + CN^- \rightarrow NiCN^+ \quad (48)$$

$$NiCN^+ + CN^- \rightarrow Ni(CN)_2 \quad (49)$$

$$Ni(CN)_2 + CN^- \rightarrow [Ni(CN)_3]^- \quad (50)$$

$$[Ni(CN)_3]^- + CN^- \rightarrow [Ni(CN)_4]^{2-} \quad (51)$$

Reduction dissociation of high valence compounds:

$$2CuO + 2H_2O + 10CN^- \rightarrow 2[Cu(CN)_4]^{3-} + (CN)_2 + 4OH^- \quad (52)$$

$$2[Ni(CN)_4]^{2-} \rightarrow [Ni_2(CN)_6]^{4-} + (CN)_2 \quad (53)$$

$$(CN)_2 + H_2O \rightarrow HOCN + HCN \quad (54)$$

Reduction of oxygen:

$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad (55)$$

Oxidation of CN^-:

$$CN^- + 2OH^- \rightarrow OCN^- + H_2O + 2e^- \quad (56)$$

Reoxidation of low valence compounds:

$$[Ni_2(CN)_6]^{4-} + 1/2O_2 + 3CN^- \rightarrow 2[Ni(CN)_4]^{2-} + OCN^- \quad (57)$$

$$2[Cu(CN)_4]^{3-} + 5O_2 \rightarrow 2CuO + 8OCN^- \quad (58)$$

Although cobalt ion is widely used as a catalyst for oxidation of organic substances, there was no indication that cobalt or a cobalt cyanide complex catalyzes oxidation of cyanide to cyanate. In the tall column test, after Cu and Ni in the effluent dropped to zero no cyanate was detected even though appreciable amounts of cobalt were present in the samples. The batch reactor using reagent grade cobalt sulfate did not show any oxidation either. The extremely high stability of $[Co(CN)_6]^{3-}$ restricts its potential as a catalyst for cyanide oxidation.

Complexation As reviewed in Chapter one, cyanide complexes with many metals. It was identified that 18 metal elements can form complexes with cyanide ion. In the case of soil, however, only Fe, Co, Ni, Cu, Zn, Cd are important. Other metals are either too scarce, like Au, Ag, Hg etc., or too stable to be complexed with cyanide, such as Al, Fe, Ca, K, and so on.

Ion chromatographic results, Figure 22(a), 22(b) and 22(C), for the effluents from the tall column indicate that there are four major absorption peaks, three of which are identified as cyanide species. The first peak is CN^-, the third is a copper cyanide complex, $[Cu(CN)_4]^{3-}$, and the forth is the nickel cyanide complex, $[Ni(CN)_4]^{2-}$. Spiking the samples with $[Fe(CN)_6]^{3-}$, OCN^-, SCN^-, and $[Co(CN)_6]^{2-}$ had no effect on the second peak, indicating that the second peak is not a common cyanide species. Further ion chromatographic analyses indicate that the second peak is nitrate resulting

from the transformation of cyanide. The absorption intensity and area under the first peak(CN^-) became smaller and smaller as the second peak increased, implying that cyanide might be transformed to the anion, NO_3^-, represented by the second absorption peak.

The data in Table XIV indicate that nickel, cobalt and copper in the effluents are all complexed with cyanide. Although nickel(II) cyanide dissolves readily in aqueous solutions of alkali metal cyanide the solubility of $[Ni(CN)_4]^{2-}$ in dilute sodium cyanide solution is limited at low pH values. That is why only a small fraction of nickel in the soil for the tall column test was found in the effluents. The soils placed in the tall column contained 109 grams of nickel, but the total nickel found in all the effluent samples is only 0.1 grams.

Precipitation Transition metals play an important role in destroying cyanide. They complex with cyanide ion to form less toxic substances, catalyze the oxidation of cyanide to cyanate, and precipitate from solution or on solids. Transition metals are particularly important in assessing the environmental fate of cyanide in soils.

The most abundant transition metals in soils are iron, copper, cobalt, zinc, nickel and cadmium. These elements can usually be leached from soil by alkaline cyanide solution forming complexes with CN^-. No work has previously been reported on the relative

importance and conditions for metallo-cyanides to precipitate on soils.

Precipitation of metal cyanide complexes depends on pH and concentration of cyanide in the solution, and the conditions of precipitation vary from metal to metal. Most metal cyanide complexes precipitate at low pH and low concentrations of cyanide. But addition of excess acid will break down some metal cyanide complex precipitates to corresponding anions and cations. While studying the recovery of cyanide from cyanide complexes, Semmens and Chang(68) observed that white zinc cyanide precipitate formed in the column during the regeneration of zinc cyanide saturated ion exchange resin, and that if enough acid was added the anionic metal cyanide complexes of zinc and cadmium can completely break down to form Zn^{2+}, Cd^{2+} and HCN:

$$[Zn(CN)_4]^{2-} + 4H^+ \rightarrow Zn^{2+} + 4HCN \quad (59)$$

$$[Cd(CN)_4]^{2-} + 4H^+ \rightarrow Cd^{2+} + 4HCN \quad (60)$$

Precipitation was studied using both column test with soils and stirred tests with reagent grade chemicals. Cyanide solution of 130 ppm CN^- was made from reagent grade sodium cyanide. Metal cyanide solutions were prepared by adding 200 ppm metal in the form of copper oxide (CuO), zinc oxide(ZnO), nickel chloride($NiCl_2.6H_2O$), and cadmium chloride ($CdCl_2$) to an alkaline sodium cyanide solution. Sulfuric acid was used to adjust the pH of the solutions,

ranging from 1 to 13. After the solution pumping was stopped and the effluent stopped dripping from the bottom of the column, the column was cut into four sections. Duplicate solid samples(50 grams each) were taken from each section. Each sample was washed with 250 mL solutions of varying pH ranging from 1 to 13. The wash slurry was filtered and the filtrate analyzed for elemental concentrations using ICP and metallo-cyanide concentrations with ion chromatography. Tests for pure chemicals were conducted in a one-liter glass vessel which was immersed in a temperature bath maintained at 30°C. For each test one liter of cyanide solution with 130 ppm CN^- and 200 ppm metal was added into the reactor which was then stirred. Different pHs of the initial solution were tested for every chemical. After equilibrium was obtained, separation of the precipitate from the solution was carried out by ultrafiltration. Solution samples were analyzed for free cyanide using the distillation-colorimetric method(8) and metallo-cyanide complex using IC. The precipitate was redissolved in alkaline solution (pH=13) and analyzed for metal, total cyanide, and metallo-cyanide complexes.

(1) Complexation of Transition Metals in Soil with Cyanide

Analyses of the effluents from the tall column using ICP indicated that only copper, nickel and cobalt were present in the effluent solution in appreciable amounts. Figure 14 shows the change of the concentration of these elements with pore volume of cyanide solution passed through the column. Although iron, zinc and

cadmium were present in the soil, these elements were absent from the effluents. Knowing that $[Cu(CN)_4]^{3-}$, $[Ni(CN)_4]^{2-}$ and $[Co(CN)_6]^{4-}$ are the most stable species for Cu, Ni, and Co in cyanide solution, we found that all these elements in solution were complexed with cyanide, shown in Table XIV.

(2) Precipitation of Metallo-Cyanide Complexes in Soils

Metallo-cyanide precipitates on soilds were washed out using alkaline solutions. The solutions were analyzed for both metal element and metallo-cyanide complex concentrations. Data showed that only nickel, zinc and cadmium cyanide precipitated in the soil. For each solid sample wash solutions with different pH values were used. Table XV indicates the effect of pH of the wash solution on concentration of the precipitated metal cyanide complex in the wash filtrate.

These data suggest that precipitation of the complexes occurs in specific pH ranges as shown in Figures 34-36. Since copper cyanide precipitates only under acidic conditions(pH<3), no copper cyanide precipitate was found in any wash solution of the solid samples.

Iron was not leached from the soil. The soil used for the tall column test has 0.0066% total sulfur and 4.5% iron. These data indicate that iron in the soil exists in an oxide form, not as a

sulfide. This study suggests that cyanide does not react with iron in hematite, which is consistent with Sheridan's discovery. When studying the effect of ore type, depth, and leach time on cyanide species in column tests using NaCN leach solution, Sheridan(69) found that the concentration of $[Fe(CN)_6]^{4-}$ was the lowest with an oxide ore. The big difference of total sulphur content between the soil(0.0066%) used for this study and the ore(0.18%) used in Sheridan's work may be the reason why some iron was detected in the column effluents in his columns, but not in this study.

(3) Precipitation of Metallo-cyanide Complexes in Reagent Grade Chemical Solutions.

Precipitation of metallo-cyanide complexes depends on pH and concentration of cyanide in solution, and the conditions of precipitation vary from metal to metal. Beacuse soil is such a complex system, precise conditions for each metallo-cyanide complex to precipitate can only be identified by studying the behaviors of the complexes in pure chemical solutions. Table XVI lists the results for reagent grade ZnO, $CdCl_2$, $NiCl_2.6H_2O$, and CuO in sodium cyanide solution.

It may be seen from the data in Table XVI that the pH of the solution plays an extremely important role for metallo-cyanides to precipitate. The results show that CuCN precipitates at very low

pH, below 3. Further addition of sulfuric acid did not break down the CuCN precipitate, (Figure 39). For zinc and cadmium, however, $Zn(CN)_2$ and $Cd(CN)_2$ were found to dominate in different pH ranges. Figure 37 indicates that $Zn(CN)_{2(s)}$ forms only at pHs between 3 and 9, and the maximum precipitation occurs in the pH range from 4 to 6. The behavior of cadmium cyanide precipitate, $Cd(CN)_{2(s)}$, is similar to that of $Zn(CN)_{2(s)}$. But cadmium cyanide precipitates in a much narrower pH range, from 4 to 8, than that of zinc cyanide, (Figure 38). Nickel cyanide precipitates only at low cyanide concentration. At high CN^- concentration $Ni(CN)_{2(s)}$ does not form regardless of pH, (Figure 40). That is why precipitation of nickel cyanide occurred in the column test with soil, but not in the stirred test with pure chemicals.

Adsorption/Ion Exchange From an environmental standpoint, the need to understand the factors moderating the partition of ions between solid surface and aqueous solutions is of considerable importance. Generally, soil particles have together a net negative charge. But iron- and aluminum-rich soils can attain a positive charge at low pH, but such cases are rare. "It is nonetheless a fact that most anions are held strongly by the soil complex"(70). The adsorption of an anion onto a soil surface will be governed by the properties of both the anion and the surface. Between pH 4 and pH 7 there are usually some positive charges to which anions can be attracted electrostatically on soils. Hydrous oxides generate a significant number of positive charges as the pH falls, goethite below 8-8.5,

gibbsite below 9, and silica below 2.

Studies indicated that soils having high concentrations of manganese and hydrous oxides of iron retained cyanide the most(71). Bessent et al. (72) noted that ion exchange resins do not remove free cyanide effectively. However, all metal-cyanide complexes are readily adsorbed by anion exchange resins.

Under the conditions for this study, a minimum pH of 7 for the effluent coming out from the soils, silica does not have the chance to generate positive charges. But, the gibbsite, hematite(73), goethite and kaolinite existing in the soil all have favorable conditions for generating positive charges, and therefore, can adsorb anions. Anions are usually adsorbed on these surfaces by non-specific adsorption that balance the charge developed by the adsorption of H^+.

It is accepted that weak acid anions can be adsorbed by hydrous oxides through both specific adsorption or ligand exchange and non- specific adsorption of ions to balance the charge developed by adsorption of H^+ and OH^-(74). When sodium cyanide solution percolates through soil and the pH of the solution decreases, most of the cyanide in solution exists as a weak acid, HCN(Figure 1). At pH values where the acid is fully dissociated, specific adsorption occurs only to the extent of positive charge of the surface and little specific adsorption is found at pH values more alkaline than

the zero point of charge(ZPC). With incompletely dissociated acids, anion adsorption can also take place at pH values more alkaline than the ZPC, providing the pH is somewhere near a pK_a value of the acid, where the energy required to abstract a proton from the acid is at a minimum. The proton is required for the removal of a surface OH which provides a site for the anion(75).

When the ions in solution do not have specific affinity for the metal atoms of the surface, the surface will adsorb H^+ and OH^-. If H^+ is adsorbed in excess of OH^-, the surface will have a net positive charge which is balanced by adsorption of the spectator anion from solution.

Even when the surface is negatively charged, undissociated acid molecules can be adsorbed as long as they can dissociate at the surface to provide protons which react with surface OH^- of neutral sites to form water which is readily displaced by the anion.

Solid samples were analyzed for free cyanide using the distillation-colorimetric method. Approximately 11.7 per cent of cyanide was found to be adsorbed on the soils.

Transformation to Nitrate The nitrite concentration in both solution samples and solid soils is negligible. The nitrate concentration in the soil for the tall column test was 28.4 ppm, which makes totally 2.291 grams of NO_3^- in the 80640 grams of soil

placed in the column. A similar calculation shows that there is 178.368 grams of NO_3^- in the 1721.6 kilograms of soils added in the large tank.

Total NO_3^- coming out from the effluent for the tall column is 39.928 grams. Subtracting the 2.291 grams of nitrate which originally existed in the soils, we found that 37.637 grams of nitrate is formed due to the transformation of cyanide. Further calculation indicates that 37.637 grams of nitrate is produced from 24.28 grams of sodium cyanide, which is 33.62 per cent of the total cyanide in the solutions pumped into the column.

Behavior of Zinc Although the fresh cyanide solution for the large Tank #2 test had 200 ppm of zinc added as zinc sulphate, no zinc was found in the solution samples coming out from the soil. As discussed previously, nearly all the zinc was precipitated as $Zn(CN)_2$ under the experimental conditions.

Cyanide Solution Movement in Soils

After the cyanide solution was pumped into the top center of the tank it started moving both horizontally and vertically. Under unsaturated conditions the situation is similar to infiltration, an important and widely used term in soil science. Infiltration is an example of the general phenomenon of water movement in porous media.

The concept of soil water movement as a diffusion phenomenon implicit in Buckingham's approach(76), and later in that of Gardner's(77) and Richards'(78), was explicitly proposed by Childs(79,80), who studied the hypothesis of constant diffusivity. Since the diffusivity varies greatly with moisture content, this approach can be considered only a rough approximation. Later, Childs and Collins(81) developed the concentration-dependent diffusivity by applying Darcy's law to the movement of water down a potential gradient produced by a moisture gradient.

Klute(82), following rather closely the approach of Richards, applied the continuity requirement to the vector form of Darcy's law for a homogeneous medium and derived the following equation

$$\frac{\partial \theta}{\partial t} = \nabla . (K \nabla \Phi) \qquad (2)$$

Where ∇ is the vector differential operator, K the hydraulic conductivity, θ the water content, and Φ the total potential. Philip(83) accepted equation (2) with an assumption that the total potential comprises purely gravitational and negative pressure components, and obtained equation (3)

$$\frac{\partial \theta}{\partial t} = \nabla \cdot (K \nabla \psi) + \frac{\partial K}{\partial Z} \qquad (3)$$

Where Ψ is the pressure potential and Z is the vertical ordinate. If Ψ and K are only θ-dependent functions, equation (3) becomes

$$\frac{\partial \theta}{\partial t} = \nabla \cdot (D \nabla \theta) + \frac{\partial K}{\partial Z} \qquad (4)$$

where the diffusivity D is given by Equation (5):

$$D = K \frac{\partial \psi}{\partial \theta} \qquad (5)$$

Applying equation (4) for horizontal movement of cyanide solution we have the following

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} (D \frac{\partial \theta}{\partial x}) \qquad (6)$$

Suppose the soil has a uniform initial moisture content θ_i and the center of the tank(x=0) was saturated as soon as cyanide solution was pumped into the tank, then equation (6) has the following boundary conditions:

$$\theta = \theta_i \text{ at } t=0 \quad x>0$$
$$\theta = \theta_o \text{ at } x=0 \quad t \geq 0 \qquad (7)$$

Equation (6) subject to equation (7) can be treated by Boltzmann transformation

$$\varphi = x t^{1/2} \qquad (8)$$

Substituting (8) into (6) we obtain (9)

$$-\frac{\varphi}{2}\frac{d\theta}{d\varphi} = \frac{d}{d\varphi}\left(D\frac{d\theta}{d\varphi}\right) \qquad (9)$$

Multiplying both sides of equation (9) by $d\varphi/d\theta$ gives (10)

$$\varphi d\theta = -2Dd\left(D\frac{d\theta}{d\varphi}\right) \qquad (10)$$

integrating equation (10) we obtain (11)

$$\int_{\theta_i}^{\theta} \varphi d\theta = -2D\frac{d\theta}{d\varphi} \qquad (11)$$

with $\theta=\theta_o$, $\varphi=0$.

Equation (11) can be solved by finite difference methods. Using the experimental data we obtain the relationships between advancement of the horizontal wet front and the square root of time for both large tanks:

$$\text{Tank \#1} \quad x = 1.273t^{1/2}$$
$$\text{Tank \#2} \quad x = 1.2916t^{1/2} \qquad (12)$$

where x is in units of millimeters and t in hours. The least square method fitting of equation (12) is excellent with a correlation coefficient of 0.985 for tank #1 and 0.998 for tank #2, Figures 45

and 46.

To determine how the experimental equation (12) fits the theoretical model, we develop an approximate analytical solution of equation (6), instead of using a numerical solution of equation (11). In equation (8), x can be expressed as

$$x = \varphi(\theta) t^{1/2} \tag{13}$$

The problem is to find $\varphi(\theta)$ from which the wet front at time t can be obtained by multiplying it by $t^{1/2}$. It has been shown that D is a function of θ

$$D(\theta) = -\frac{1}{2} \frac{d\varphi}{d\theta} \int_{\theta_i}^{\theta} \varphi(a)\, da \tag{14}$$

It is possible to consider a variety of functions φ and deduce D very simply from equation (14) by analytical or numerical integration. By this method one could in principle build up a large table of D as function of θ for various $\varphi(\theta)$. Then in an actual problem when D is given, one would pick out of that table the function that approximates D as a function of θ most closely and read the corresponding φ. But, this would be a tedious process.

A better way is to find an approximate analytical solution. Now, rewriting equation (6) as (15)

$$\frac{\partial x}{\partial t} + \frac{\partial}{\partial \theta}\left(\frac{D}{\partial x/\partial \theta}\right) = 0 \qquad (15)$$

Integrating equation (15) between θ and θ_o gives (16)

$$\int_{\theta}^{\theta_o} (\partial x/\partial t)\, d\theta + \frac{D(\theta_o)}{(\partial x/\partial \theta)_o} - \frac{D(\theta)}{(\partial x/\partial \theta)} = 0 \qquad (16)$$

For $\theta_i=0$, $D(\theta_i)/(\partial x/\partial \theta)_i$ is zero and (16) Reduces to (17)

$$\int_{\theta_i}^{\theta_o} (\partial x/\partial t)\, d\theta + \frac{D(\theta_0)}{(\partial x/\partial \theta)_0} = 0 \qquad (17)$$

The quantity $(\partial x/\partial t)$ is a decreasing function of θ, which is very small near saturation. Consequently for $(\theta_o-\theta)$ sufficiently smaller than $(\theta_o-\theta_i)$ we shall have (18)

$$\int_{\theta}^{\theta_o} (\partial x/\partial t)\, d\theta < \int_{\theta_i}^{\theta_o} (\partial x/\partial t)\, d\theta \qquad (18)$$

Therefore, in the region where D varies rapidly near saturation, it is reasonable to take as a first approximation (19)

$$\frac{D(\theta)}{(\partial x/\partial \theta)} = \frac{D(\theta_0)}{(\partial x/\partial \theta)_0} \qquad (19)$$

Integrating (19) and remembering that $x(\theta_o,t)=0$, we obtain (20)

$$x = -g(t) \int_{\theta}^{\theta_o} D(a)\, da \qquad (20)$$

From equation (17), we obtain (21)

$$\frac{1}{g}\frac{dg}{dt} = \int_{\theta_i}^{\theta_o} \theta D(\theta)\, d\theta \qquad (21)$$

Where the boundary condition g(0)=0. Hence (22) results

$$g^2 = 2t \Big/ \int_{\theta_i}^{\theta_o} \theta D(\theta)\, d\theta \qquad (22)$$

Substituting (22) into (20) gives (23)

$$x = \sqrt{2t} \int_{\theta}^{\theta_o} D(a)\, da \Big/ \left[\int_{\theta_i}^{\theta_o} D(a)\, da\right]^{\frac{1}{2}} \qquad (23)$$

It is evident that x is a function of the square root of time, which is consistent with the experimental equation (12).

Assessment of Soil Potential to Degrade Cyanide

As discussed above, cyanide degrades in soils via six major mechanisms. The relative importance of each mechanism depends on the characteristics of the soil used. Each mechanism has its own requirements and favored conditions.

Soils with high alumina and hydrous oxides con[illegible] such as kaolinite, feldspar, gibbisite and geothite, are able to degrade cyanide through adsorption and ion exchange. Electrostatic attraction is important for adsorption of cyanide on soils with sufficient positively-charged surface sites.

Oxidation of cyanide to cyanate occurs in those soils which have catalysts for the oxidation. Possible catalysts in soils are nickel, copper, and organic carbon. Oxidation can also be achieved through biological processes.

Low soil pH favors two mechanisms, volatilization and precipitation. Since at pHs below 7 essentially all cyanide in aqueous solution exists as hydrogen cyanide, volatilization increases as pH drops. Zinc cyanide completely precipitates at pH below 8.5. Nickel cyanide precipitates at pH lower than 8. The pH value of cyanide waste solution, especially the gold mining effluents, is usually 10 or above. Therefore, for volatilization and precipitation to play important roles in cyanide degradation in soils, soil pH should be low enough to neutralize the cyanide solution. This study indicates that if soil pH is around 7.5 or below both volatilization and precipitation will be appreciable.

Transition metals such as Cu, Ni and Zn in soils are important elements for cyanide degradation. They degrade cyanide through complexing and precipitation. The role of iron in soils is determined by its form. Iron existing as hematite does not react with cyanide. Other forms of iron may complex with cyanide. Since heavy metals are considered hazardous elements for ground water one should encourage precipitation of cyanide complexes of these metals rather than let them percolate down with solution to the water table. Therefore, close monitoring of pH is important.

Volatilization of cyanide in soil should not be highly recommended because for volatilization to be important the soil must have a high porosity. But, in high porosity soils the vertical movement of cyanide solution could be so fast that the rates of other degradation reactions can not compete with it, resulting in the possibility of cyanide percolation into ground water.

All in all soils have a tremendous ability to degrade cyanide. For example, in the tall column test even after ten pore volumes of cyanide solution percolated through the soil cyanide concentration in the effluent was still negligible.

CONCLUSIONS

This study found that minerals with high alumina or organic carbon contents tend to attenuate cyanide. The major mechanism for this kind of attenuation is adsorption with a first-order rate. The calcareous and siliceous minerals do not adsorb cyanide.

Soils, particularly those high in alumina, transition metals and/ microorganisms, and low in pH, have tremendous ability to attenuate cyanide through six major mechanisms: volatilization, oxidation, complexation, precipitation, adsorption/ion exchange, and oxidation to cyanate and ultimately to nitrate.

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Soils, particularly those high in alumina, transition metals and/ microorganisms, and low in pH, have tremendous ability to attenuate cyanide through six major mechanisms: volatilization, oxidation, complexation, precipitation, adsorption/ion exchange, and oxidation to cyanate and ultimately to nitrate.

The amount of volatilization is restricted by many factors such as soil pH, surface area available for volatilization, temperature, concentration of cyanide, and reactivities of soil components with cyanide.

Under normal conditions(ambient temperature and atmospheric pressure) oxidation of cyanide in aqueous solution by dissolved oxygen is impractically slow unless enhanced by catalysts. Organic carbon and metallo-cyanide complexes, $[Ni(CN)_4]^{2-}$ and $[Cu(CN)_4]^{3-}$, are found to catalyze the oxidation of cyanide in soils.

Precipitation of metallo-cyanide complexes is almost solely controlled by pH. Every metal element has its own specific range of pH values at which precipitation occurs. This study found that the pH range for zinc-cyanide and cadmium-cyanide complex precipitation are three to nine and four to eight respectively. A little $[Ni(CN)_4]^{2-}$ was found, but no copper-cyanide precipitate was detected.

Metallo-cyanide complexes found in the effluent from the soil column are $[Cu(CN)_4]^{3-}$ and $[Ni(CN)_4]^{2-}$. Iron as hematite in the soils was not leached out by or complexed with cyanide. All the copper and nickel in solution were complexed with cyanide. A substantial amount of zinc and cadmium were complexed with cyanide, but did not exit with the effluent due to precipitation.

Transformation into cyanate and ultimately nitrate constitutes the major part of cyanide degraded, as much as thirty three per cent of the cyanide pumped into the column.

Soils with high content of hydrous oxide behave as a anion exchanger to adsorb the cyanide ion. Free cyanide does not move far from its source in soil due to fast attenuation reactions.

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Table XIX. Data for the Tall Column Test

Pore Volume	pH	CNO(ppm)	Ni(ppm)	Co(ppm)	Cu(ppm)
0.531	7.93	1.69	1.70	0.93	0
0.541	8.05	2.10	2.16	1.24	0
0.551	8.20	2.43	2.44	1.29	0
0.566	7.98	3.05	2.93	1.32	0
0.581	8.07	4.79	3.15	1.49	0
0.601	8.09	5.58	3.24	1.52	0
0.614	8.18	6.33	3.34	1.60	0
0.626	8.19	6.52	3.50	1.72	0
0.646	8.24	6.83	3.67	1.81	0.13
0.657	8.20	7.02	4.09	1.99	0.20
0.665	8.14	7.23	4.83	2.23	0.36
0.678	8.15	7.42	4.56	2.01	0.85
0.685	8.11	7.01	4.13	1.94	1.09
0.687	8.16	6.62	3.82	2.00	1.11
0.695	8.14	6.01	3.13	1.94	1.09
0.702	8.13	5.47	3.26	1.89	1.23
0.741	8.13	5.07	3.30	1.78	1.25
0.750	8.15	4.68	3.31	1.84	1.20
0.768	8.17	4.05	3.00	1.74	1.40
0.779	8.16	3.59	2.91	1.91	1.73

Table XIX(continued)

Pore Volume	pH	CNO(ppm)	Ni(ppm)	Co(ppm)	Cu(ppm)
0.798	8.21	3.37	2.28	1.54	1.98
0.804	8.19	3.04	2.26	1.50	2.01
0.811	8.20	2.85	2.22	1.48	2.38
0.836	8.18	2.53	2.02	1.36	2.56
0.841	8.24	2.31	1.58	1.04	2.47
0.853	8.33	1.76	1.78	1.23	2.04
0.863	8.30	1.38	1.46	1.07	1.67
0.876	8.28	1.05	1.42	1.13	1.33
0.883	8.21	0.80	1.33	1.16	1.00
0.896	8.23	0.79	1.29	1.10	0.78
0.906	8.23	0.63	0.95	0.98	0.68
0.926	8.24	0.59	0.79	0.87	0.45
0.951	8.26	0.48	0.84	0.98	0.36
0.967	8.20	0.43	0.77	1.13	0.23
0.981	8.21	0.40	0.67	1.00	0.16
1.004	8.19	0.36	0.56	1.08	0.14
1.027	8.10	0.23	0.54	1.00	0.05
1.053	8.08	0.15	0.42	1.11	0.00
1.074	8.14	0.16	0.34	1.11	0.00
1.096	8.08	0.11	0.33	1.01	0.00

Table XIX. (Continued)

Pore Volume	pH	CNO(ppm)	Ni(ppm)	Co(ppm)	Cu(ppm)
1.121	8.15	0.080	0.31	1.07	0
1.143	8.13	0.080	0.23	1.07	0
1.174	8.01	0.060	0.18	0.94	0
1.224	7.95	0.040	0.13	0.90	0
1.262	7.96	0.010	0.11	0.84	0
1.279	7.93	0	0.09	0.94	0
1.311	7.80	0	0.08	0.73	0
1.330	7.95	0	0.09	0.70	0
1.355	7.97	0	0.07	0.85	0
1.375	8.03	0	0.05	0.82	0
1.398	8.06	0	0.06	0.76	0
1.419	8.05	0	0.04	0.74	0
1.436	7.96	0	0.03	0.69	0
1.460	8.00	0	0.01	0.690	0
1.481	7.79	0	0	0.54	0
1.504	7.85	0	0	0.53	0
1.523	7.81	0	0	0.54	0
1.539	7.78	0	0	0.50	0
1.555	7.76	0	0	0.46	0
1.575	7.73	0	0	0.42	0

Table XIX. (continued)

Pore Volume	pH	CNO(ppm)	Ni(ppm)	Co(ppm)	Cu(ppm)
1.595	7.70		0.46	0	
1.620	7.75	0	0.42	0	
1.633	7.76	0	0.39	0	
1.650	7.70	0	0.37	0	
1.666	7.70	0	0.34	0	
1.668	7.62	0	0.31	0	
1.670	7.75	0	0.27	0	
1.686	7.74	0	0.21	0	
1.709	7.75	0	0.17	0	
1.748	7.68	0	0.11	0	
1.775	7.68	0	0.05	0	
1.795	7.74	0	0	0	
1.823	7.73	0	0	0	
1.851	7.72	0	0	0	
1.881	7.76	0	0	0	
1.909	7.78	0	0	0	
1.992	7.75	0	0	0	
2.098	7.74	0	0	0	
2.209	7.69	0	0	0	
2.344	7.65	0	0	0	

Table XX. Data for Accumulated Per Cent of HCN Volatilized above the Large Tank #1 From the Concentric Rings

Time (days)	Rm=4"	Rm=12"	Rm=20"	Rm=33"	Total
5	6.22	0.03	0	0	6.25
10	6.04	0.11	0	0	6.15
15	5.88	0.35	0.008	0	6.238
20	5.42	0.54	0.011	0	5.971
25	5.25	0.88	0.079	0	6.209
30	5.01	1.03	0.320	0	6.360
35	4.84	1.34	0.660	0	6.840
40	4.66	1.77	0.970	0	7.400
45	4.24	1.98	1.210	0	7.430
50	4.11	2.13	1.430	0	7.625
60	3.89	2.34	1.670	0	7.740
70	3.66	2.59	1.910	0	7.810
80	3.43	2.78	2.080	0.003	7.423
90	3.32	2.96	2.180	0.056	7.536
100	3.19	3.11	2.350	0.089	7.499
110	3.05	3.28	2.560	0.140	7.700
120	3.00	3.48	2.700	0.340	9.520
130	2.85	3.69	2.900	0.520	9.960
140	2.75	3.85	3.070	0.740	10.41

Table XX. (continued)

Time (Days)	Rm=4"	Rm=12"	Rm=20"	Rm=33"	Total
150	2.55	4.05	2.16	1.01	10.41
160	2.45	4.26	2.30	1.22	10.85
170	2.25	4.47	2.45	1.44	11.33
180	2.20	4.59	2.58	1.54	11.71
190	2.15	4.43	2.78	1.65	11.90
200	2.00	4.23	2.94	1.87	11.82
210	1.85	4.13	3.08	2.13	11.85
220	1.75	4.03	3.18	2.30	12.03
230	1.70	3.83	3.30	2.52	12.08
240	1.65	3.67	3.47	2.74	12.20
250	1.50	3.52	3.62	2.99	12.34
260	1.45	3.36	3.80	3.21	12.41
270	1.30	3.21	3.85	3.50	12.37
280	1.25	3.16	3.80	3.71	12.16
290	1.20	3.00	3.70	3.60	12.13
300	1.05	2.85	3.55	3.48	12.64
310	1.00	2.69	3.38	3.36	12.02
320	0.85	2.48	3.12	3.22	10.55

Table XXI. Data for the Accumulated Per cent of HCN Volaytilized above the Large Tank #2 from the Concentric Rings

Time (Days)	Rm=4"	Rm=12"	Rm=20"	Rm=33"	Total
5	7.43	0.09	0	0	7.52
10	7.08	0.17	0.013	0	7.263
15	6.86	0.54	0.036	0	7.436
20	6.53	0.89	0.067	0	7.487
25	6.39	1.11	0.088	0	7.588
30	6.20	1.54	0.099	0	8.730
35	5.74	1.96	1.11	0	8.810
40	5.22	2.31	1.44	0	8.970
45	5.01	2.63	1.77	0.004	9.410
50	4.71	2.99	1.89	0.045	9.635
60	4.32	3.22	2.09	0.168	9.798
70	4.00	3.43	2.21	0.350	9.990
80	3.78	3.63	2.39	0.870	10.670
90	3.44	3.88	2.65	1.040	11.010
100	3.25	4.01	2.83	1.330	11.420
110	3.14	4.16	2.95	1.470	11.720
120	3.02	4.33	3.12	1.600	12.140
130	2.92	4.51	3.26	1.790	12.480
140	2.82	4.70	3.40	2.000	12.920

Table XXI. (continued)

Time (days)	Rm=4"	Rm=12"	Rm=20"	Rm=33"	Total
150	2.71	4.85	3.57	2.16	13.29
160	2.60	4.75	3.70	2.30	13.30
170	2.51	4.65	3.86	2.45	13.47
180	2.36	4.44	3.99	2.58	13.38
190	2.20	4.27	3.89	2.78	13.14
200	2.05	4.08	3.84	2.94	12.91
210	1.95	3.92	3.67	3.08	12.62
220	1.85	3.76	3.54	3.18	12.33
230	1.80	3.60	3.40	3.30	12.10
240	1.70	3.45	3.25	3.47	11.87
250	1.57	3.28	3.11	3.62	11.58
260	1.42	3.14	3.00	3.80	11.36
270	1.30	3.01	2.89	3.85	11.05
280	1.15	2.85	2.75	3.80	10.55
290	1.07	2.72	2.61	3.70	10.10
300	1.00	2.56	2.34	3.55	9.54
310	0.81	2.21	2.11	3.25	9.40
320	0.44	1.95	1.76	2.89	9.32

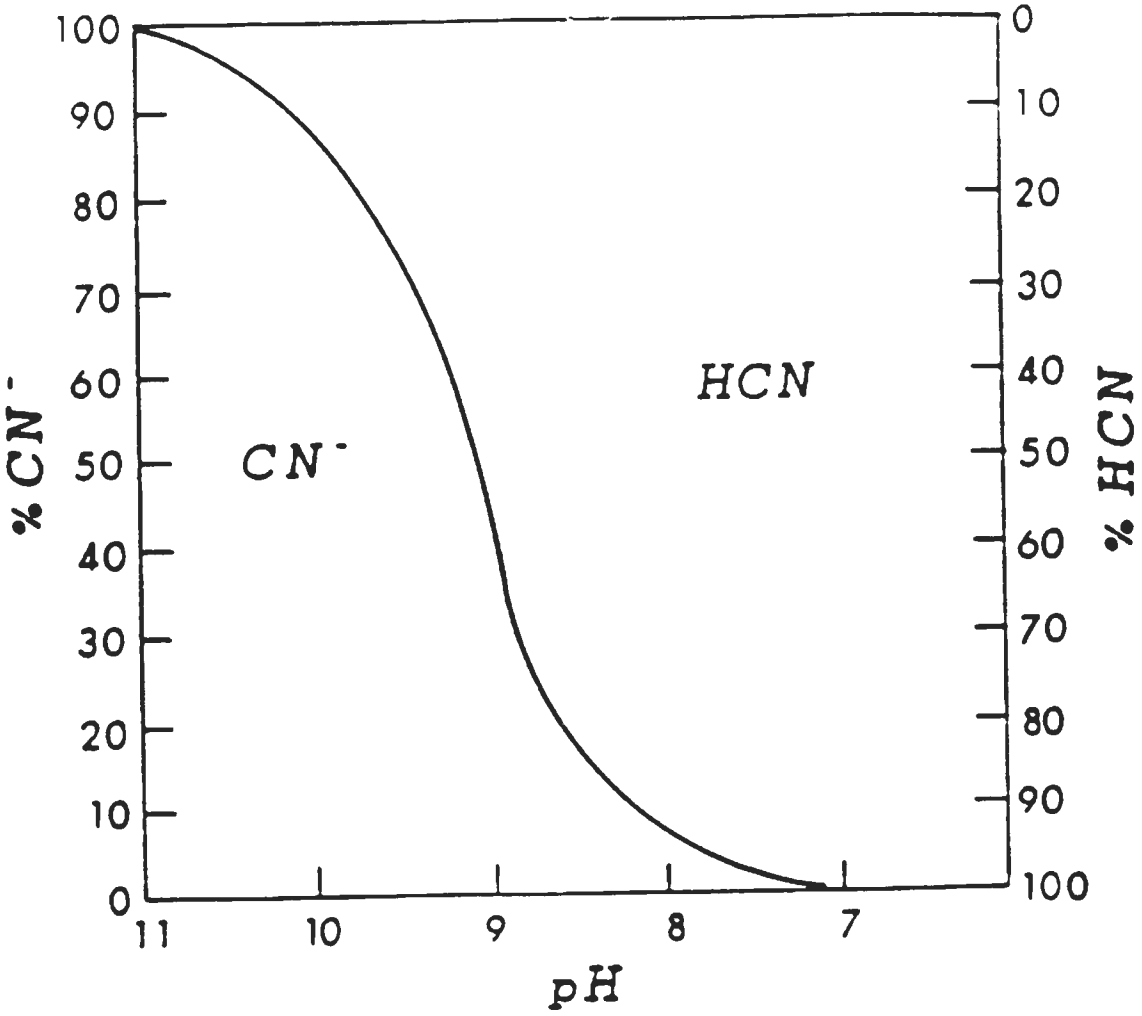


Figure 1. Effect of pH on the Equilibrium Between HCN and CN^- in Aqueous Solution

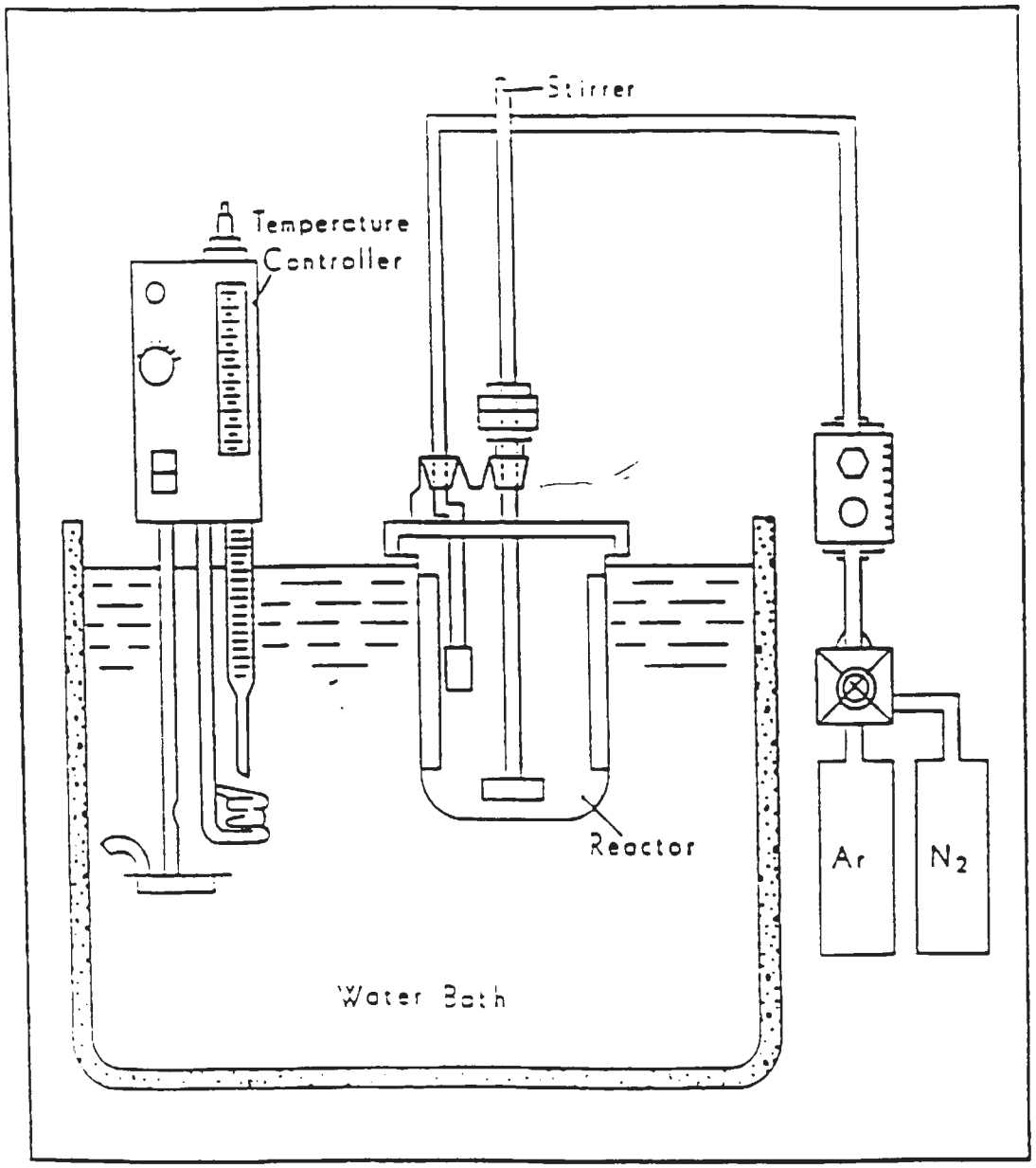


Figure 2. The Stirred Reactor

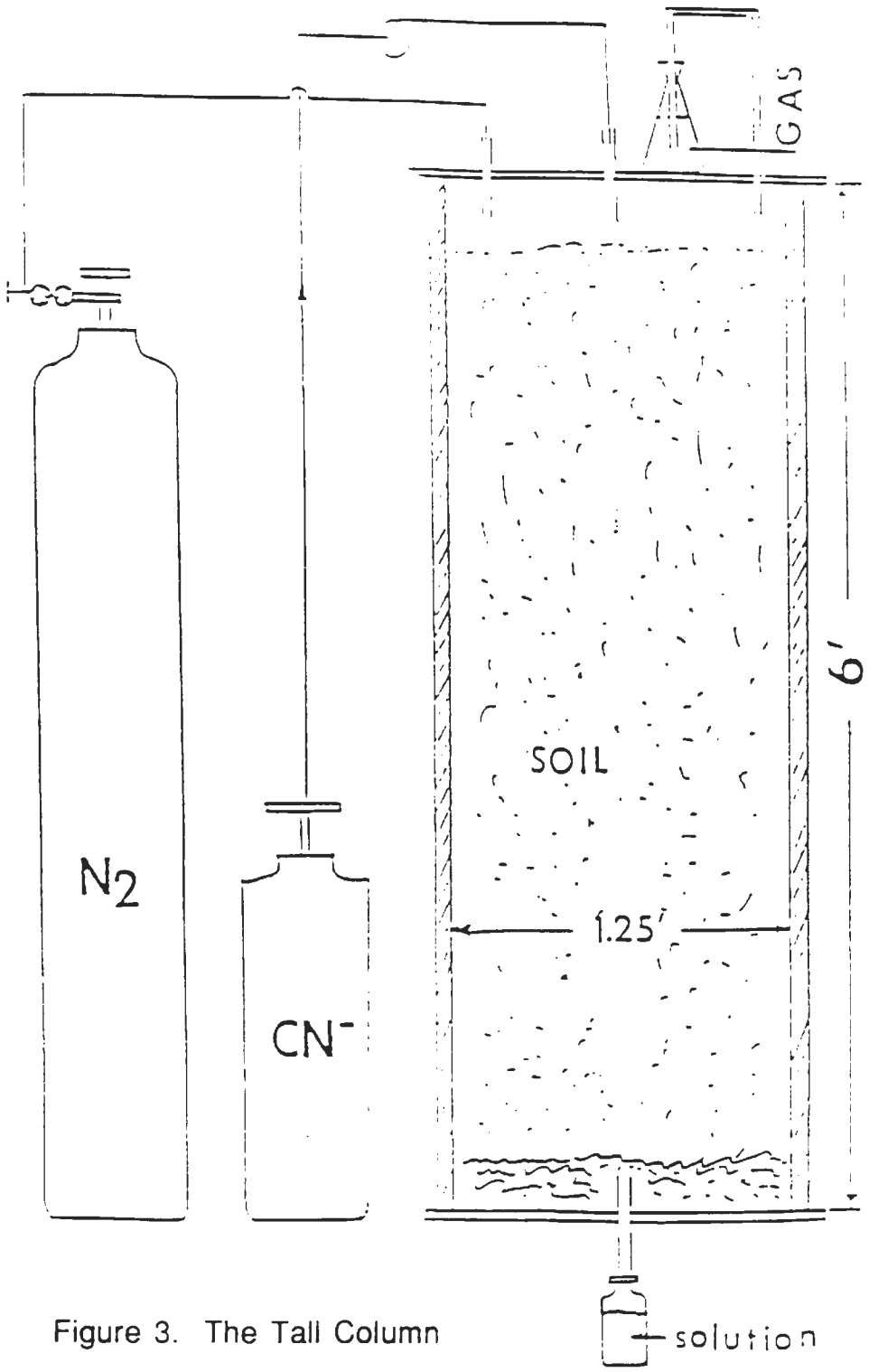


Figure 3. The Tall Column

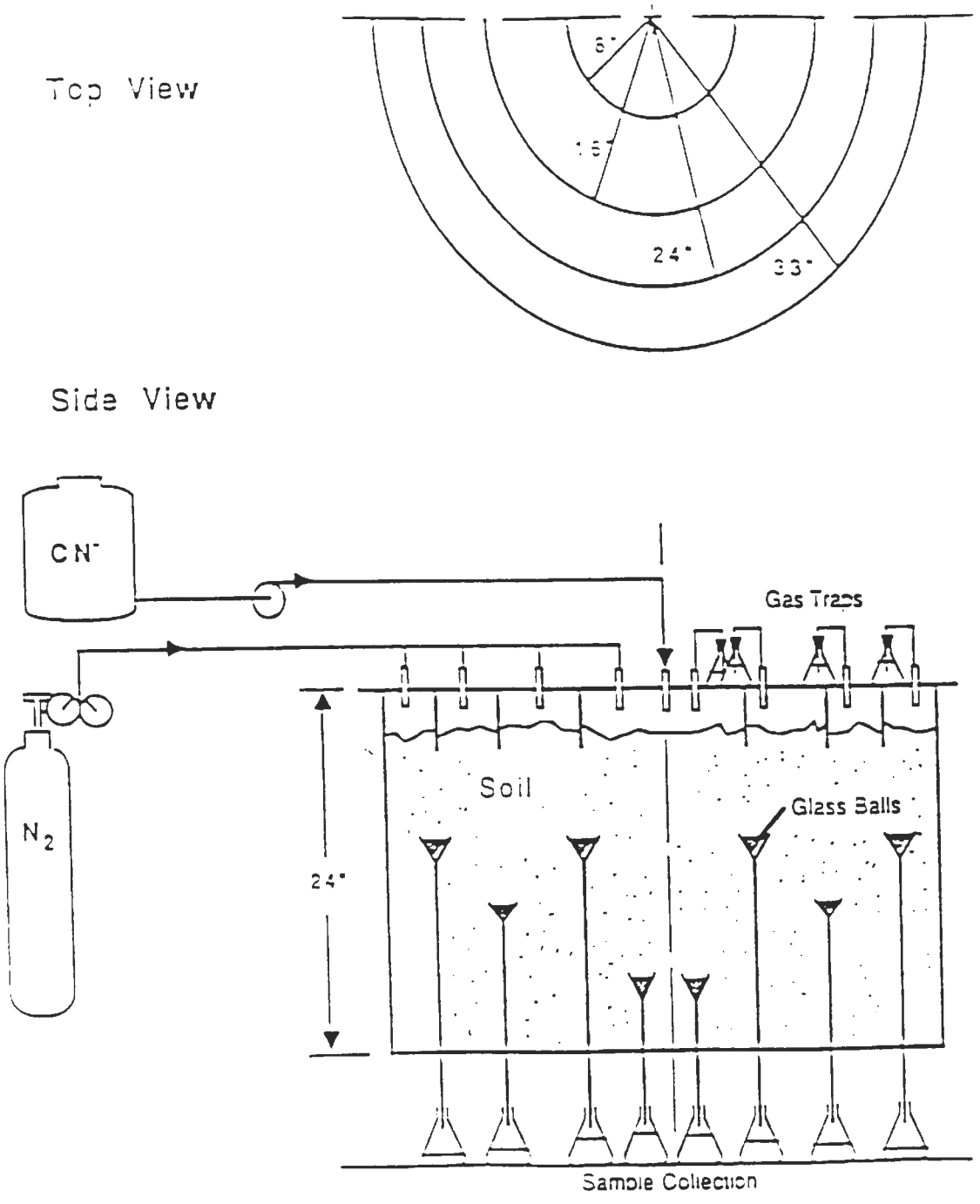
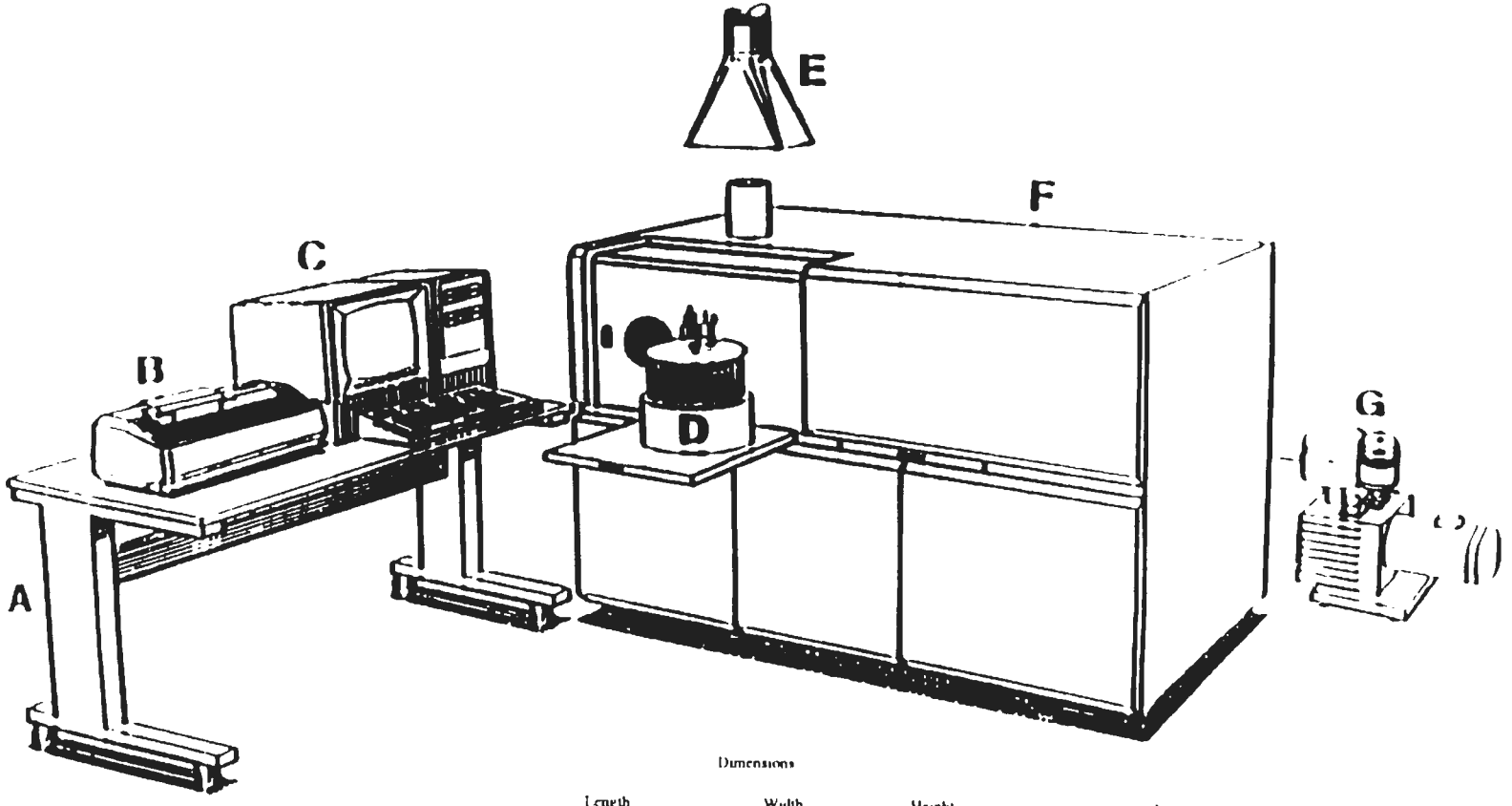


Figure 4. The Large Tank



Dimensions

	Length (cm)	Width (cm)	Height (cm)	weight (kg)
A Workstation	121 9	76 2	66	10 1
B PR 210 Printer	54 9	33	23 1	13 2
C PE 7500 computer	60	56 7	48 3	18 6
D Autosampler	33	36	33	4 5
E Vent	30 5	18 2	30 5	-
F spectrometer	196	56 1	144 6	757
G Vacuum pump	58	21 6	45 7	36 3

Figure 5. Dimensions of the Plasma II System Components

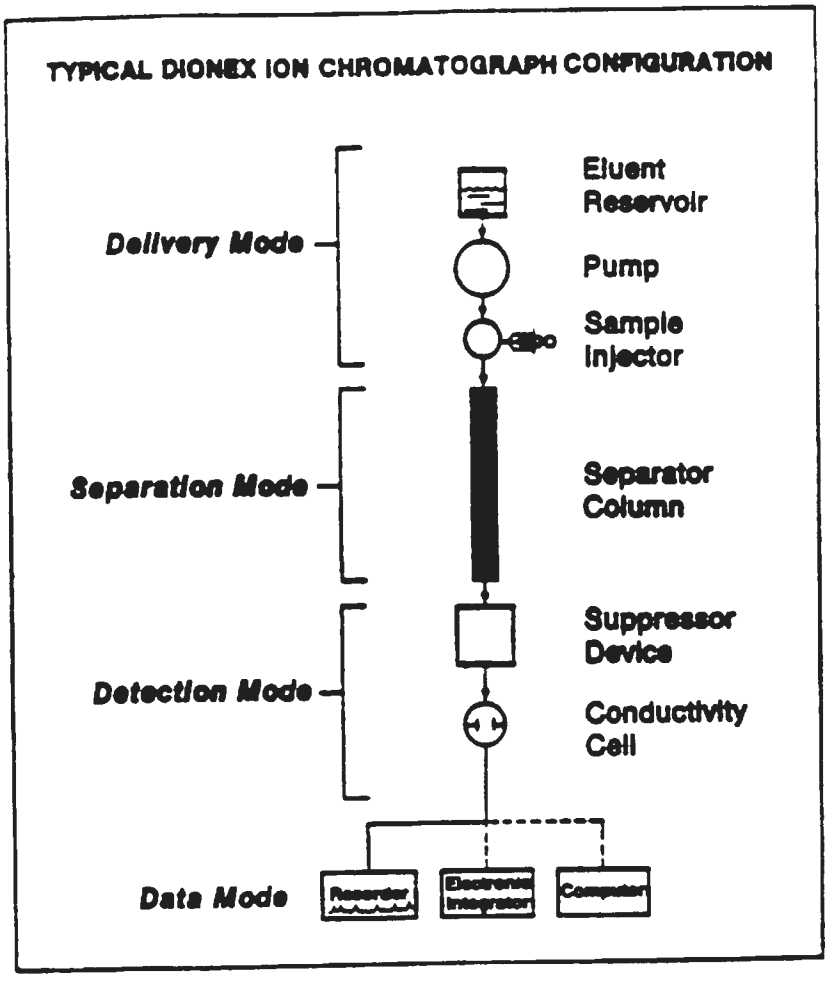


Figure 6. Schematic Diagram of the Ion Chromatograph

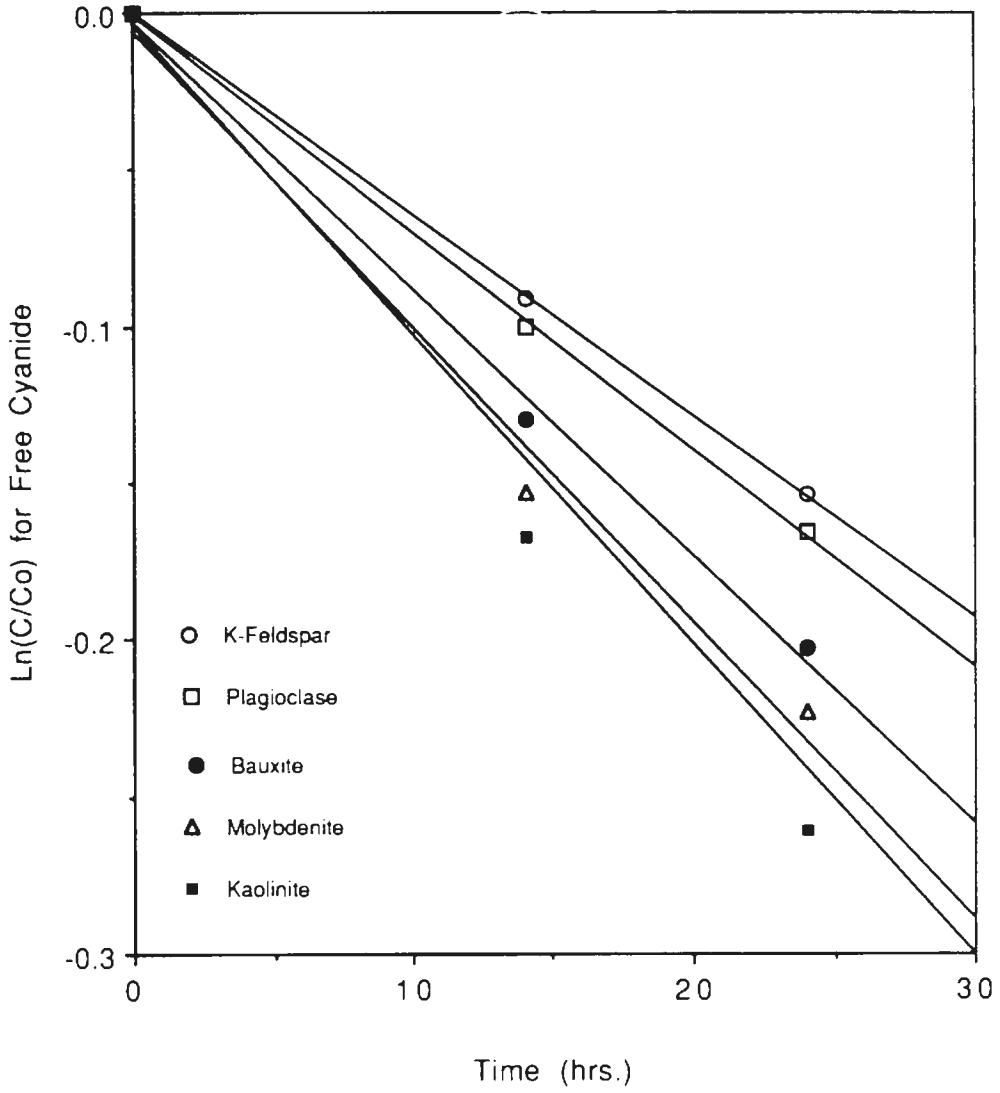


Figure 7. Plots of First-Order Fitting for Reactions of Cyanide With Pure Minerals in a Stirred Reactor

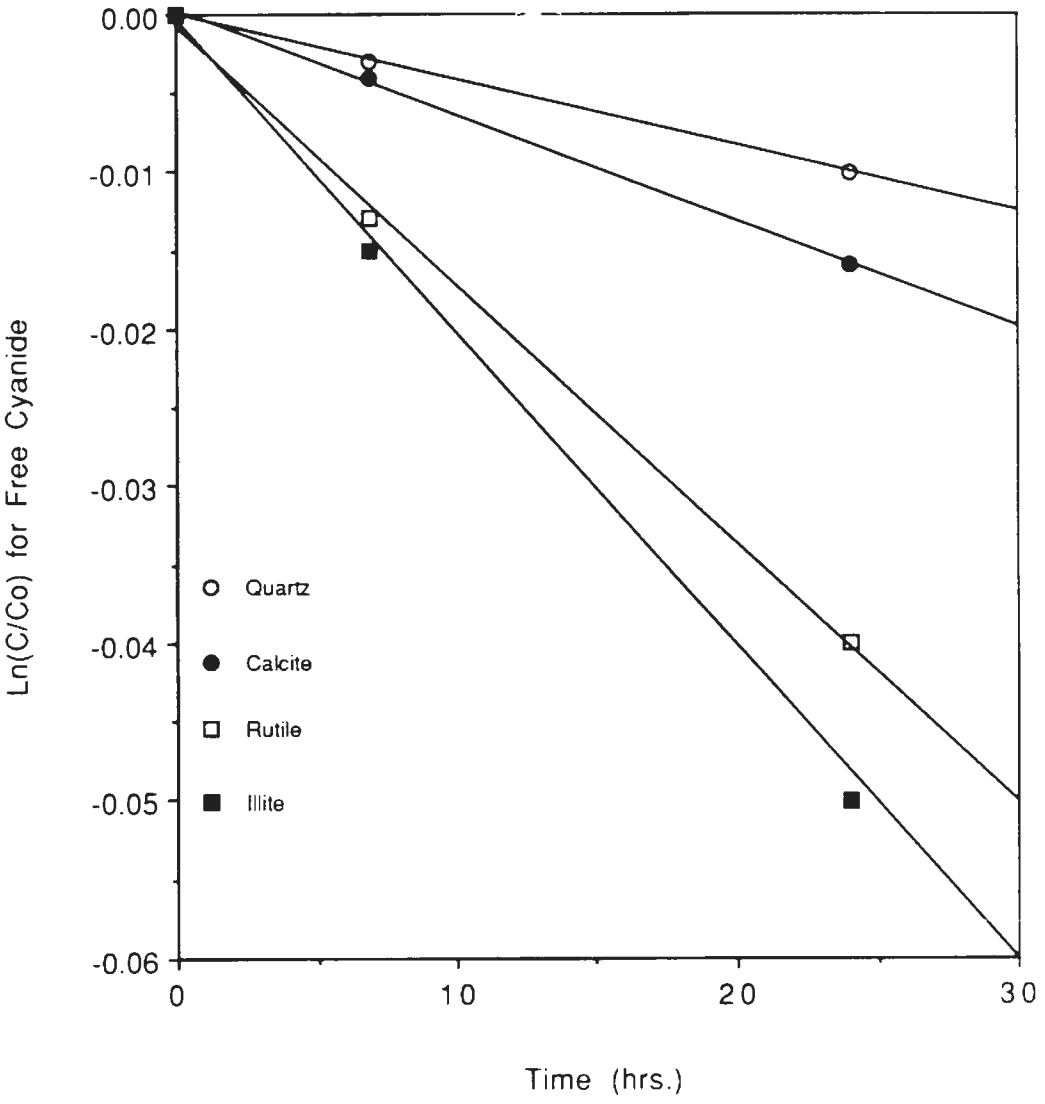


Figure 8. Plots of First-Order Fitting for Reactions of Cyanide with Pure Minerals in a Stirred Reactor

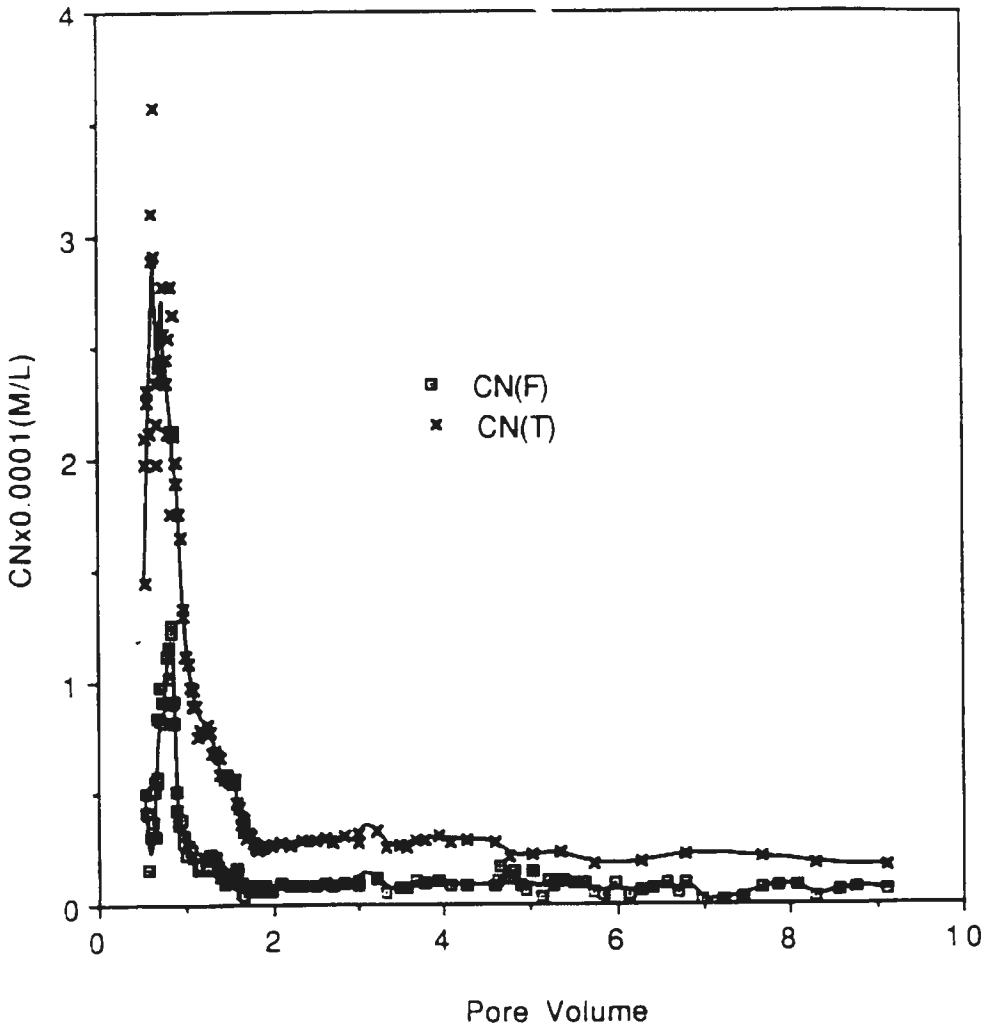


Figure 9. Concentrations of Free and Total Cyanide in the Effluent Versus Pore Volume for The Tall Column Test

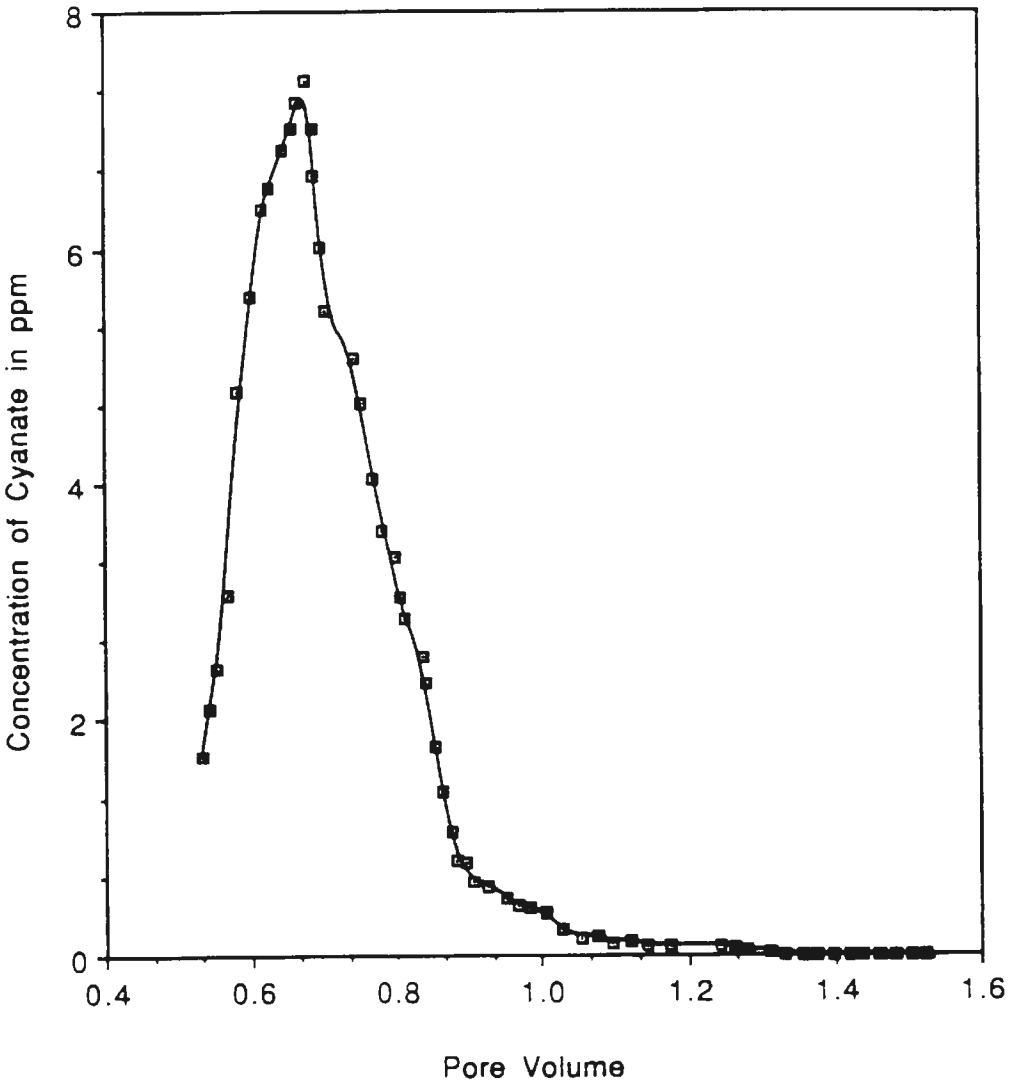


Figure 10. Cyanate Concentration in the Effluent Versus Pore Volume for the Tall Column Test

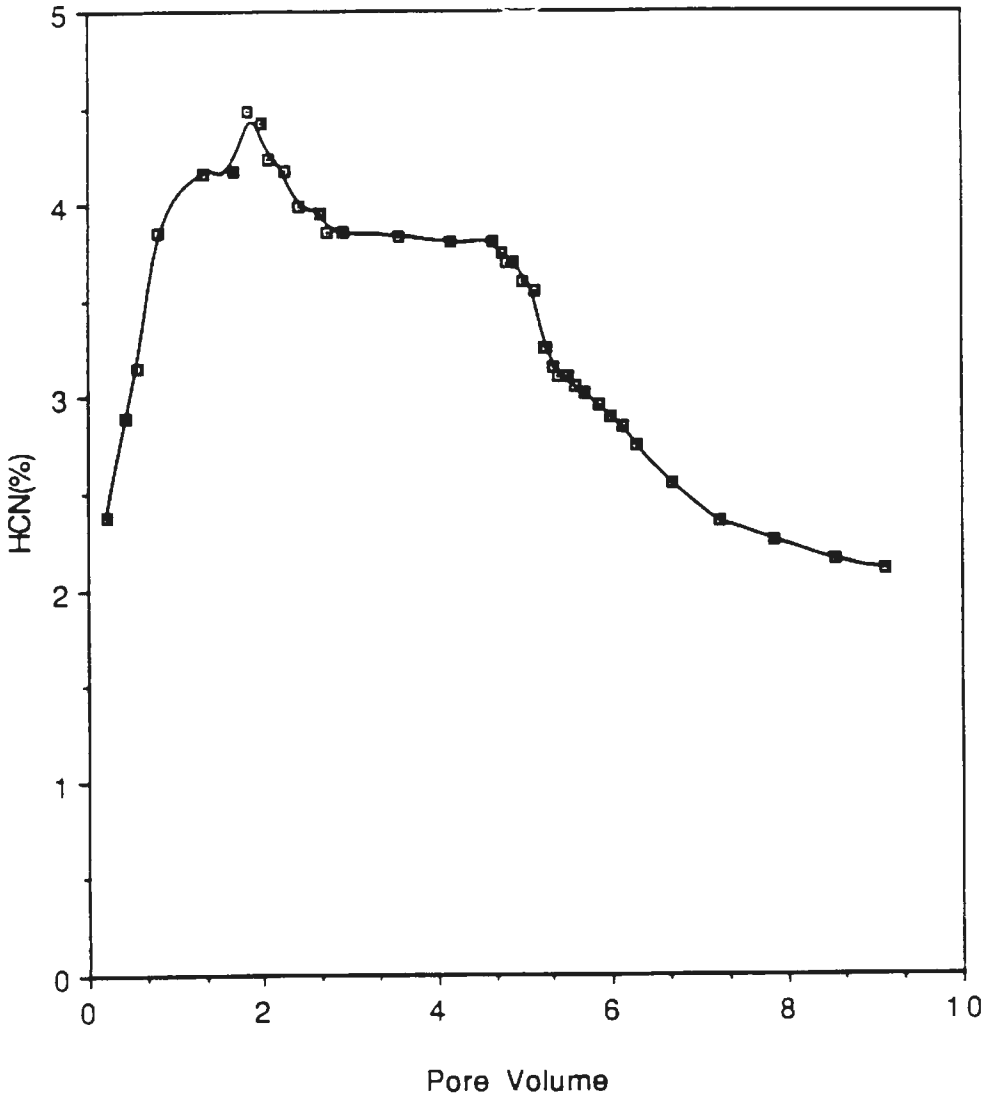


Figure 11. Per Cent of HCN Volatilized above the Tall Column

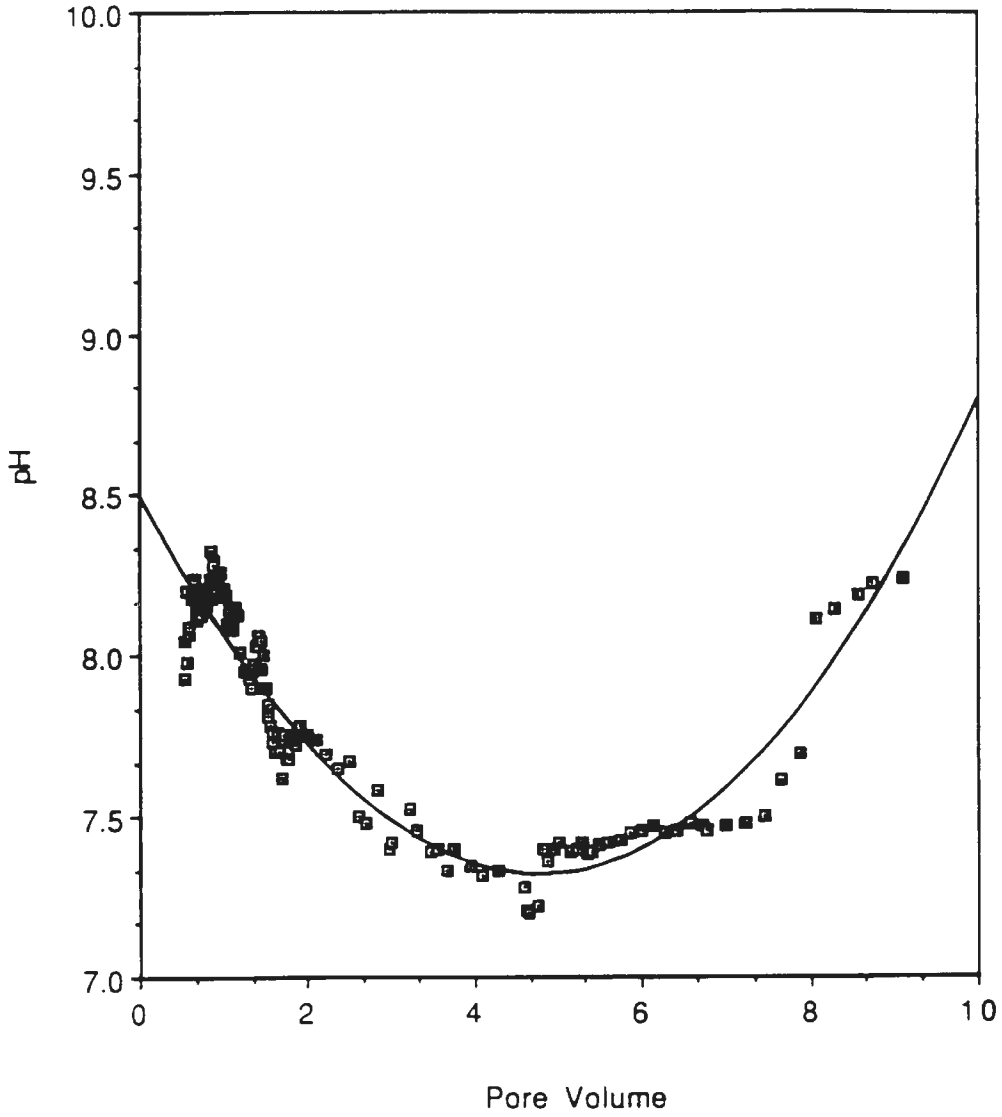


Figure 12. pH of the Effluent vs Pore Volume for the Tall Column

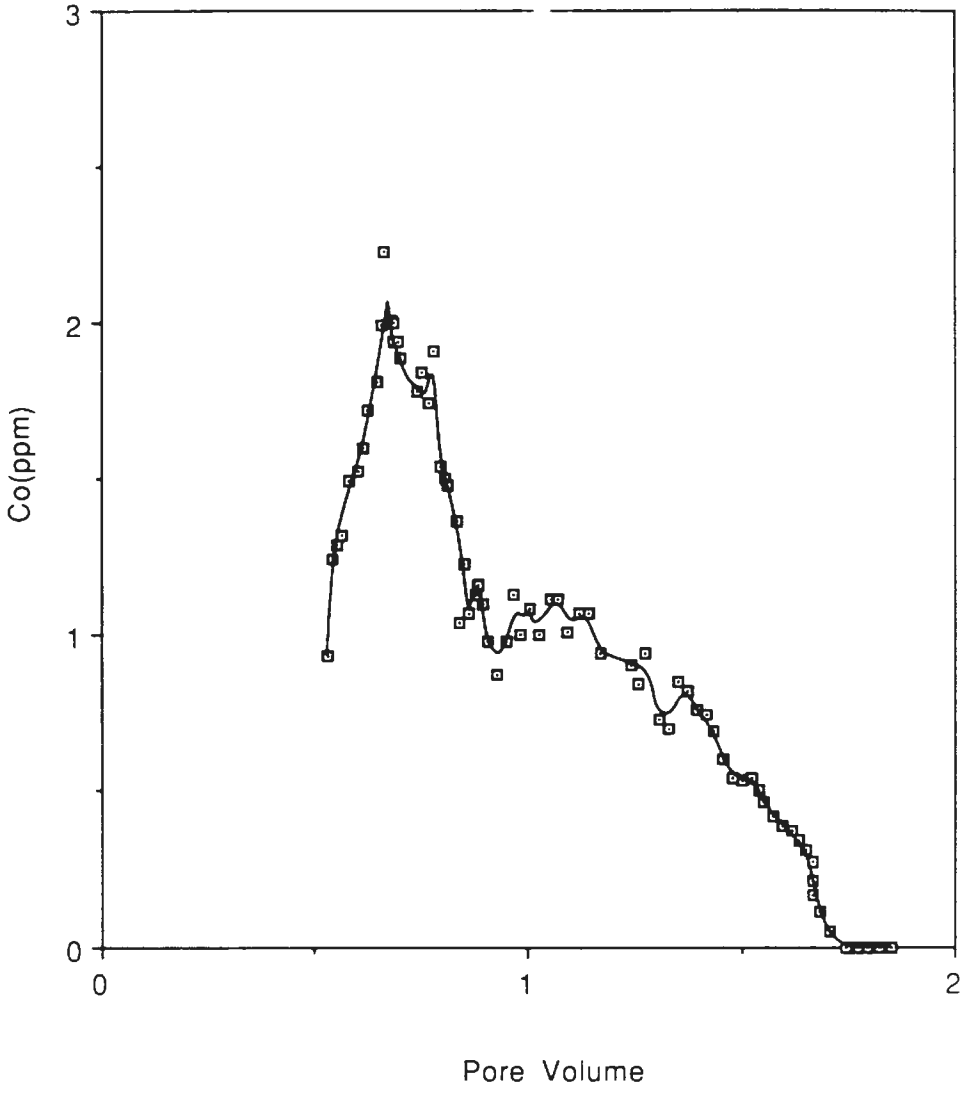


Figure 13. Concentration of Cobalt in the Effluent Versus Pore Volume for the Tall Column Test

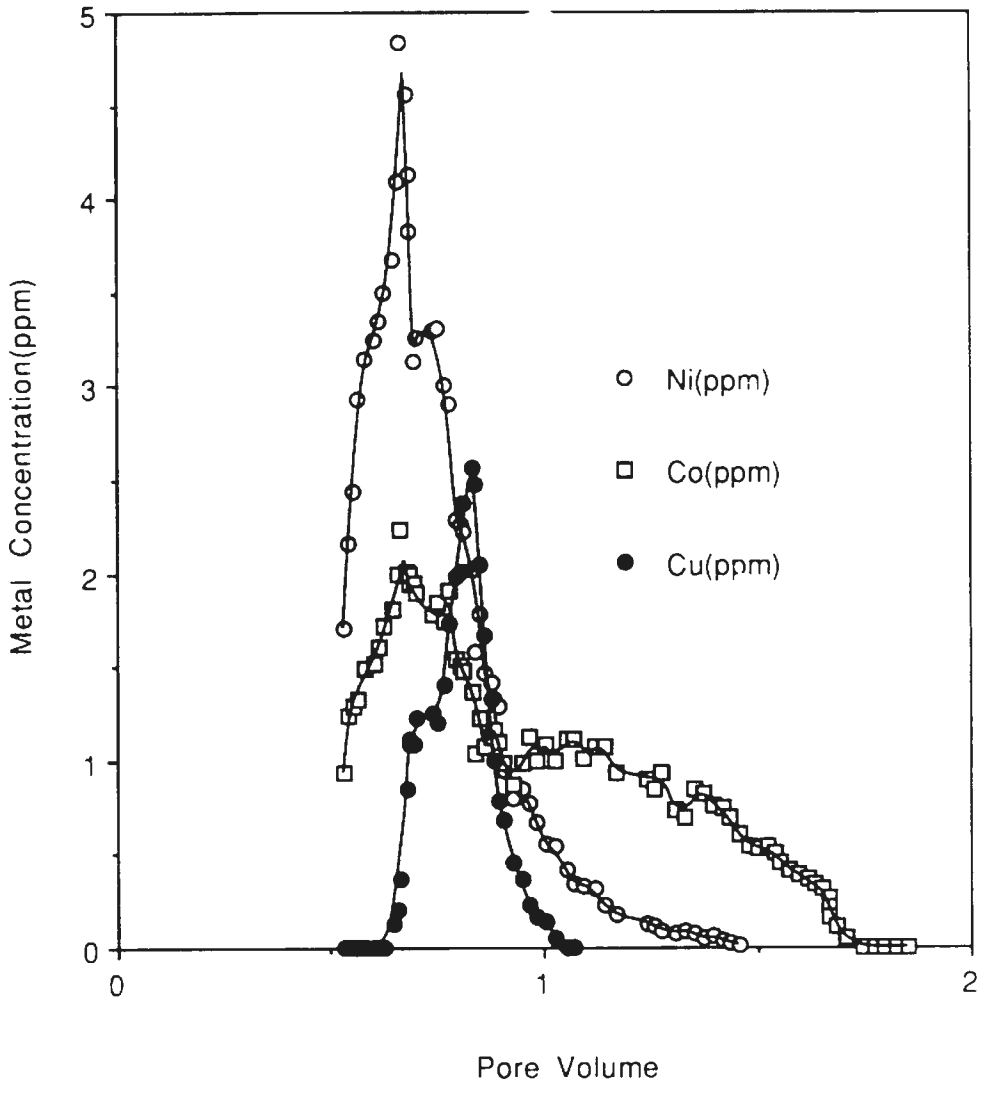


Figure 14. Concentrations of Metals in the Effluent Vs Pore Volume for the Tall Column Test

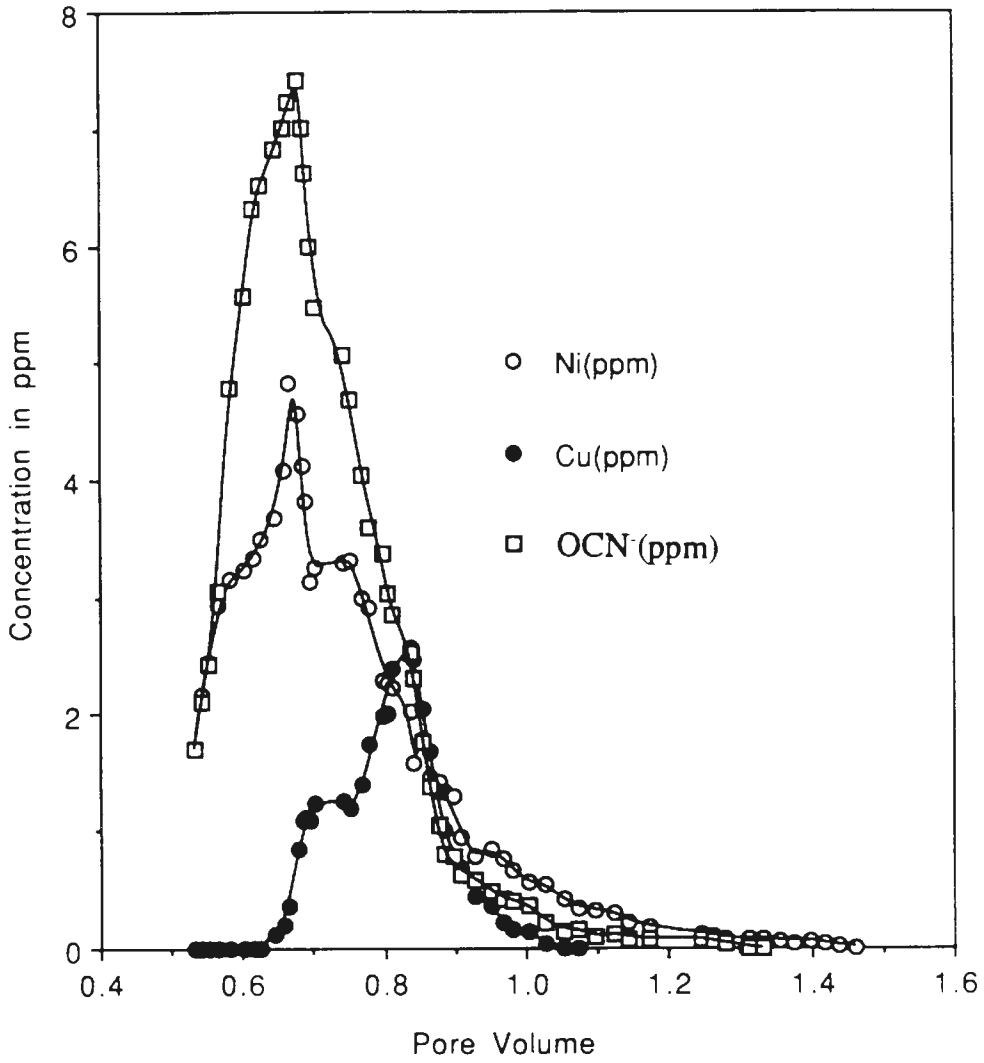


Figure 15. Concentrations of Nickel, Copper and Cyanate in the Effluent for the Tall Column Test

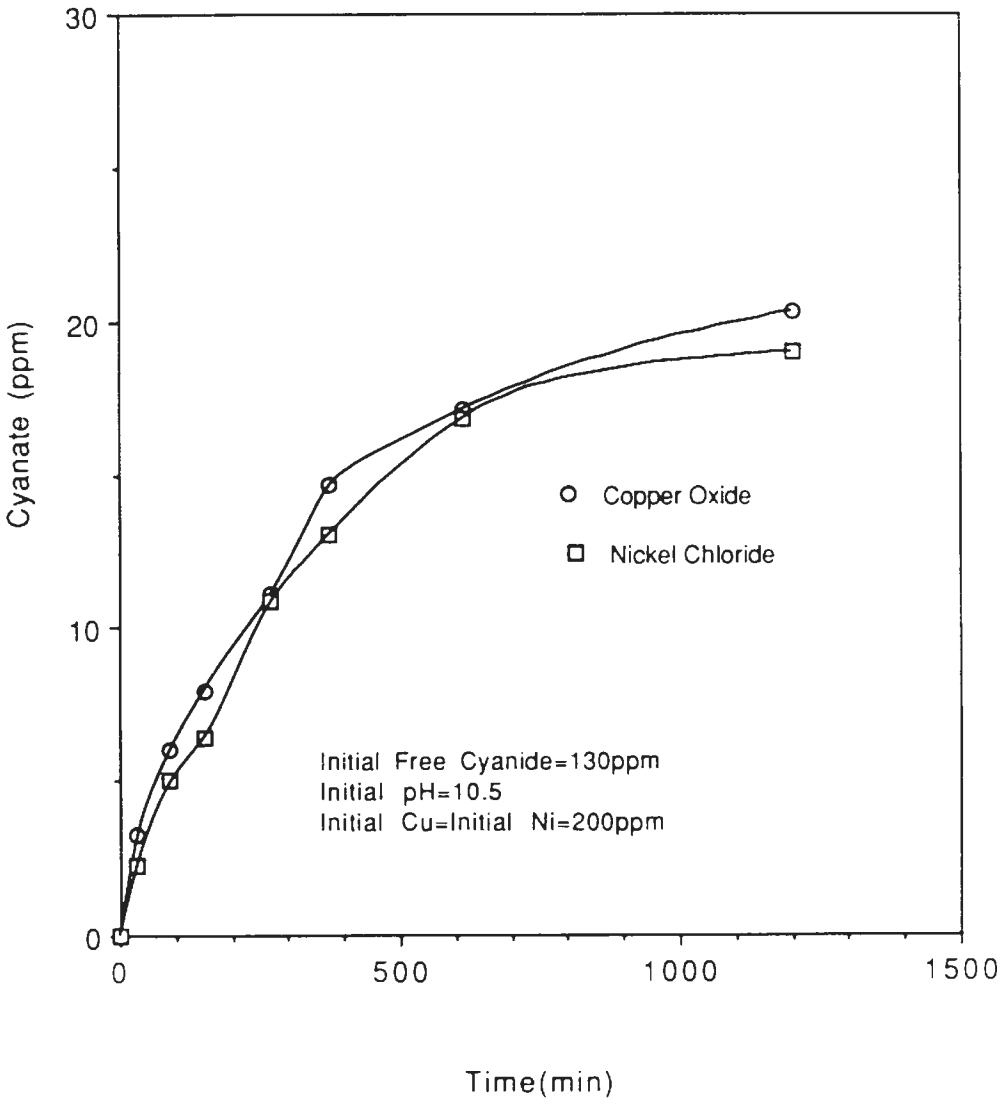


Figure 16. Cyanate Versus Time for Cu and Ni Containing Cyanide Solutions Proceeded in a Stirred Reactor

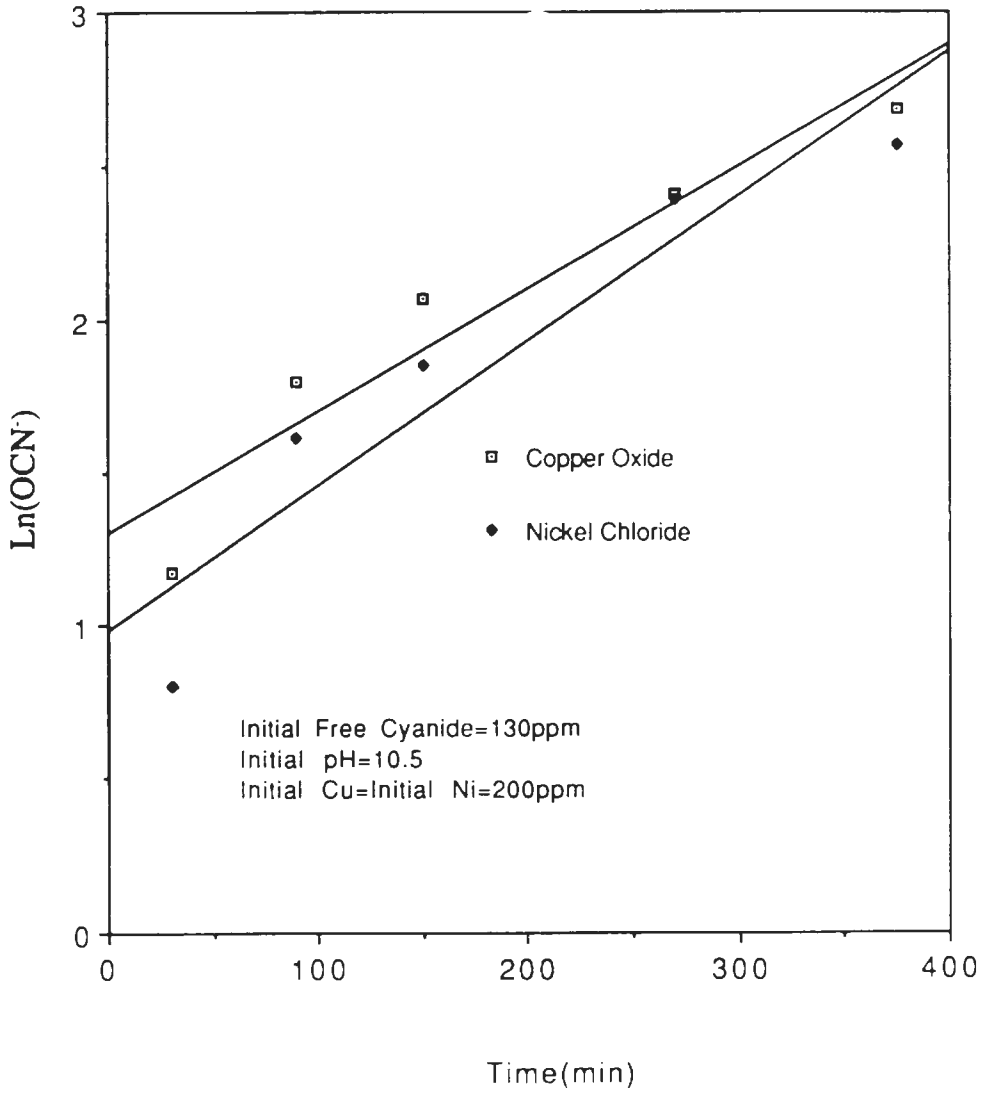


Figure 17. $Ln(OCN^-)$ Versus Time for Cu and Ni Containing Cyanide Solution in a Stirred Reactor

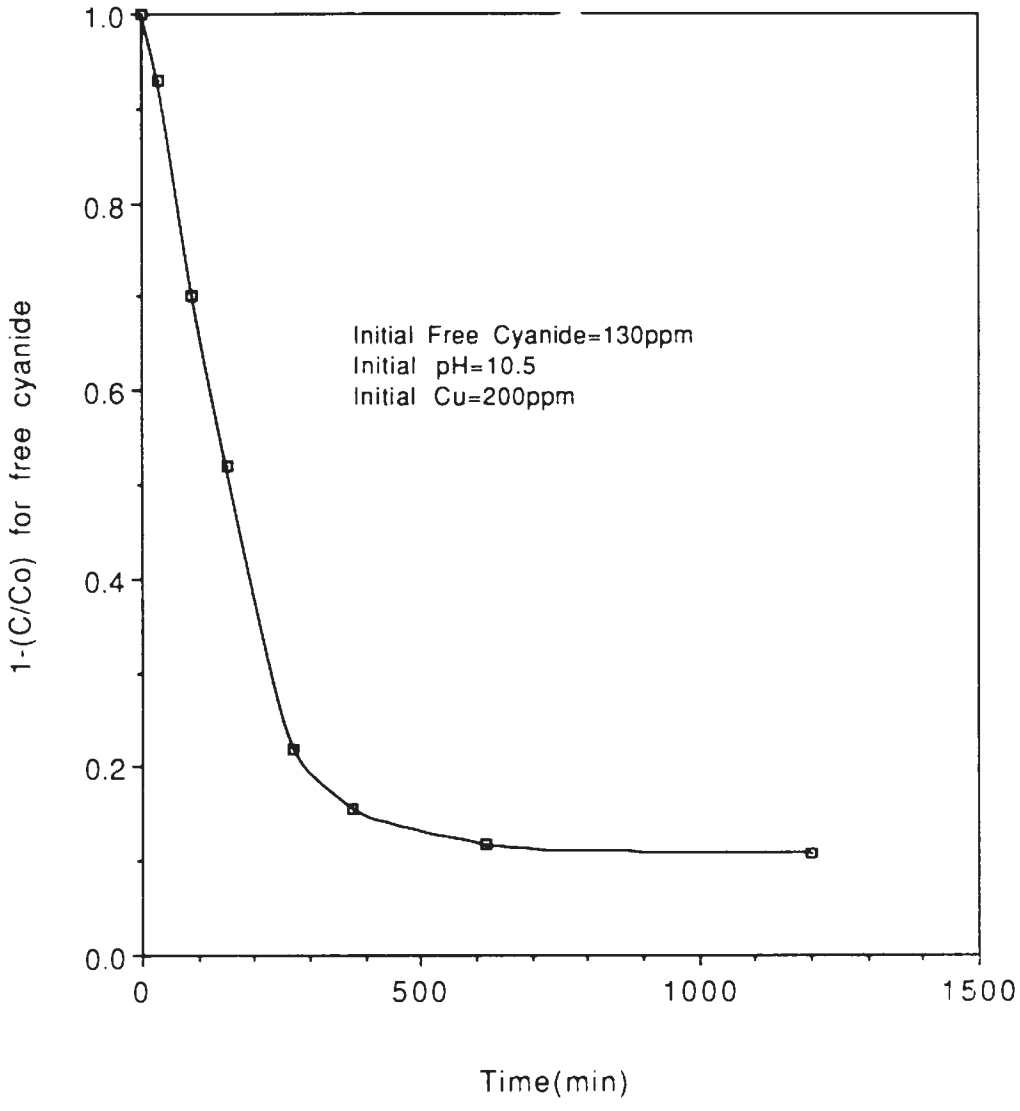


Figure 18. Rate of Cyanide Reaction for Cu Containing Cyanide Solution in a Stirred Reactor

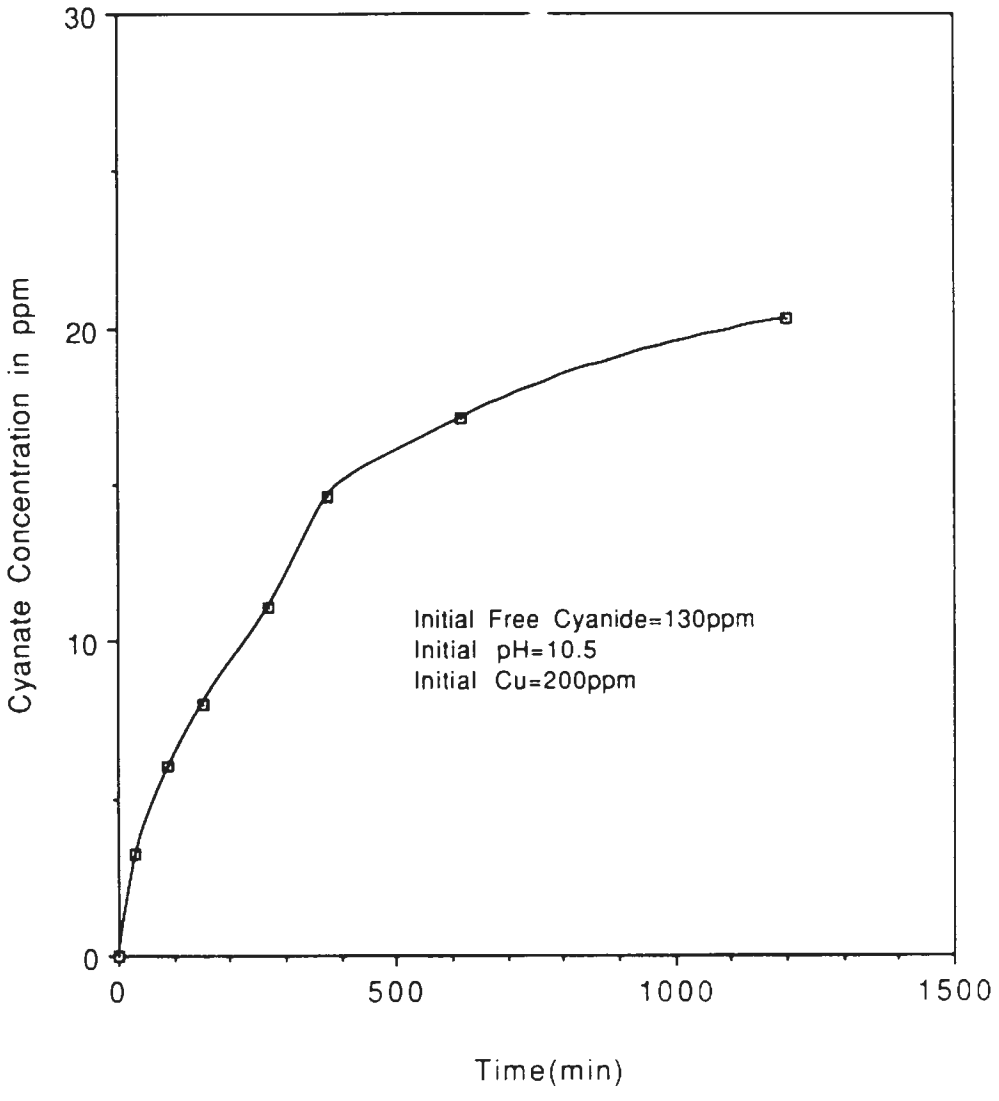


Figure 19. Cyanate Concentration vs Time for Cu Containing Cyanide Solution in a Stirred Reactor

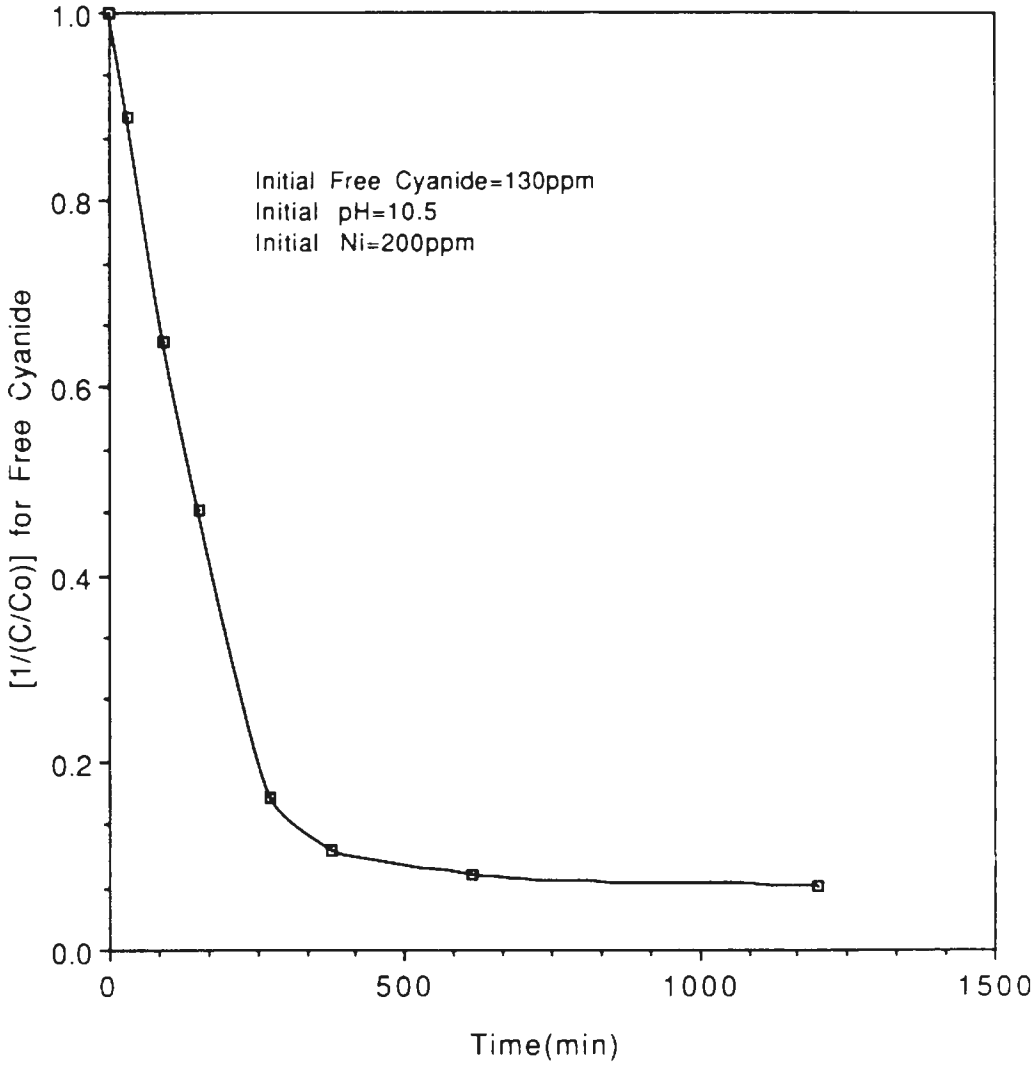


Figure 20. Rate of Cyanide Reaction for Ni Containing Cyanide Solution in a Stirred Reactor

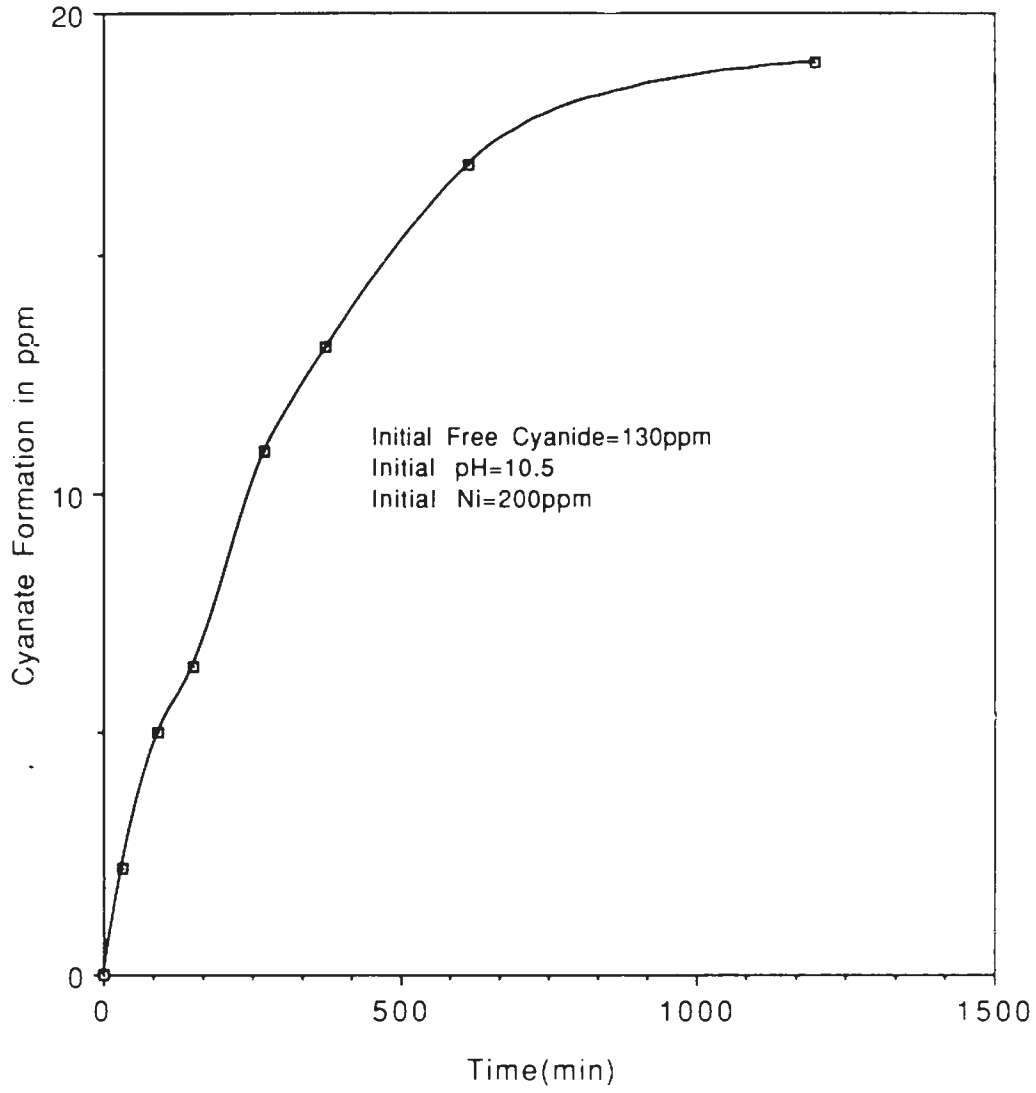


Figure 21. Cyanate Concentration vs Time for Ni Containing Cyanide Solution in a Stirred Reactor

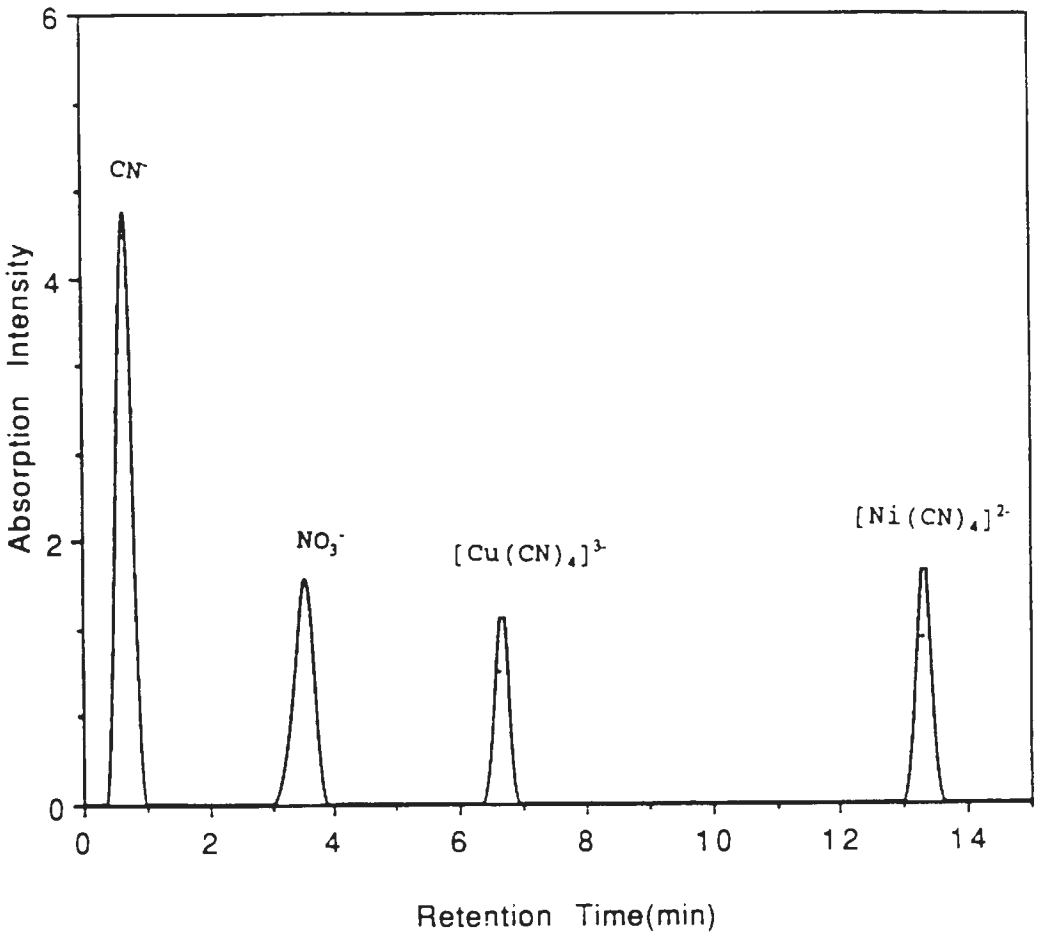


Figure 22(a). Ion-Absorption Peaks of the Effluent for the Tall Column When 0.678 Pore Volumes of Cyanide Solutions Was Added

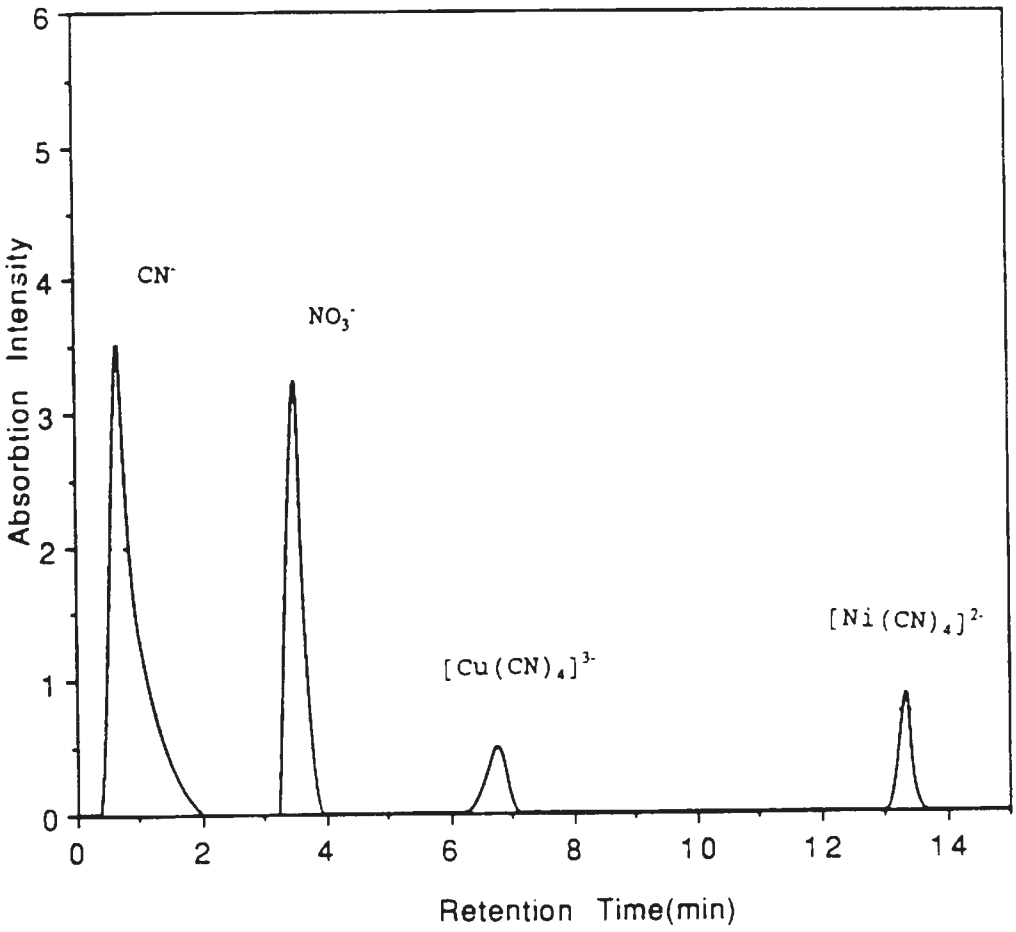


Figure 22(b). Ion-Absorption Peaks of the Effluent for the Tall Column When o.841 Pore Volumes of Cyanide Solution Was Added

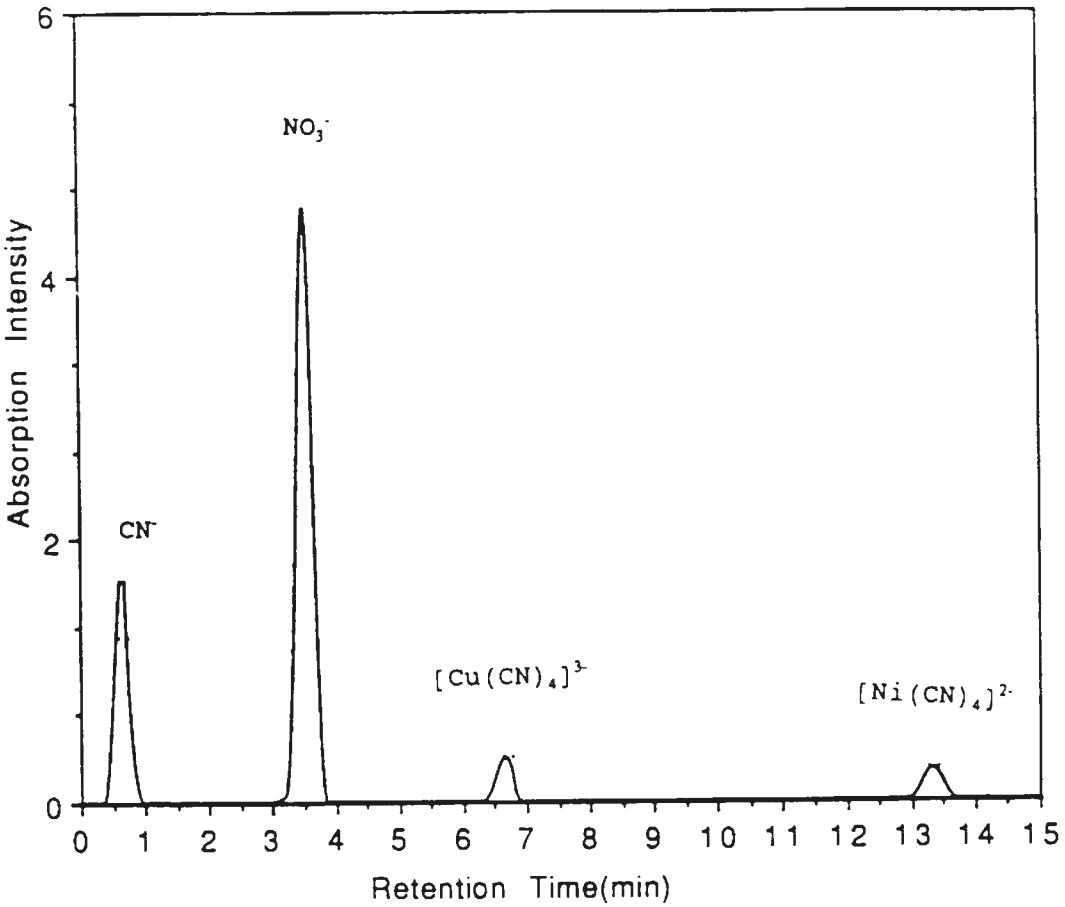


Figure 22(c). Ion-Absorption Peaks of the Effluent for the Tall Column When 1.1 Pore Volumes of Cyanide Solution Was Added

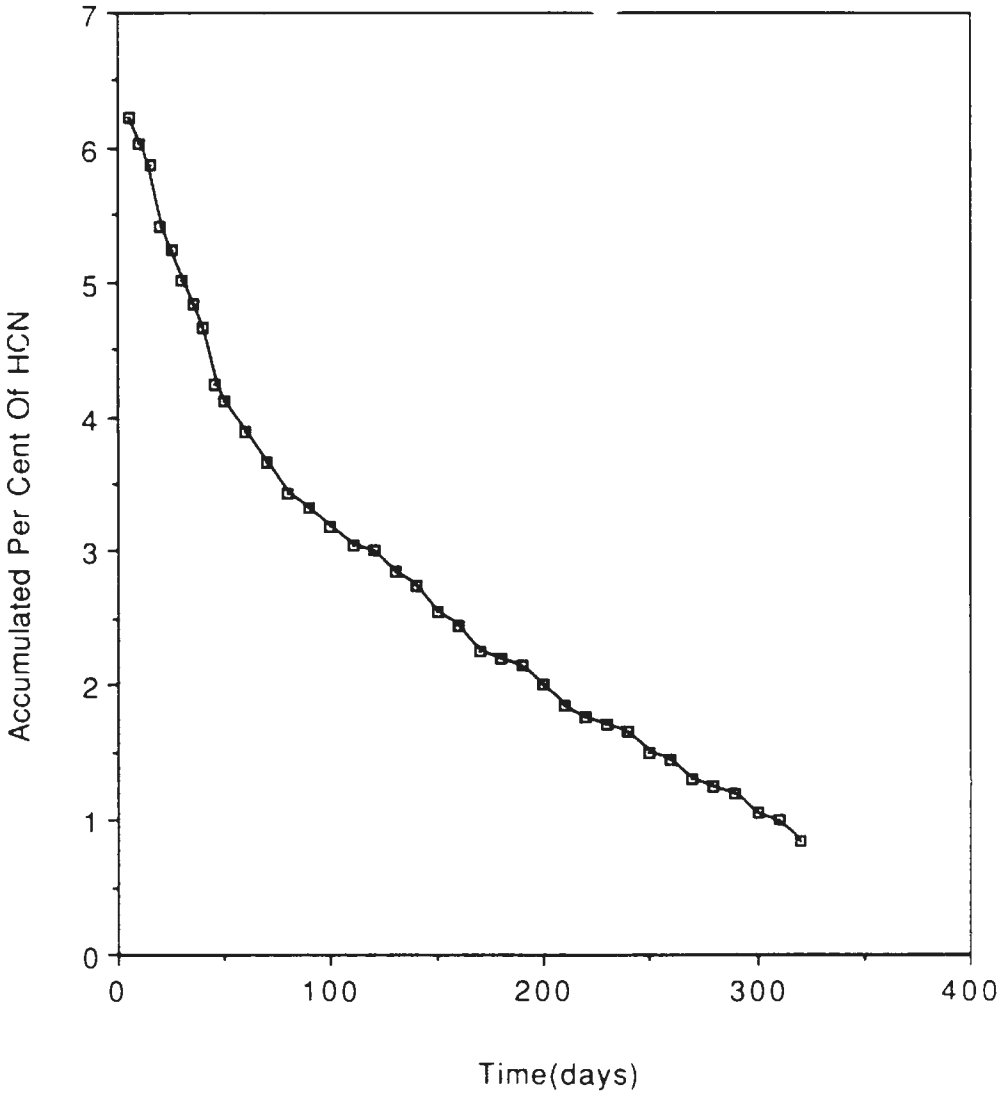


Figure 23. Per Cent of HCN Volatilized From the First Ring(r=10.16 cm) Above the Large Tank #1

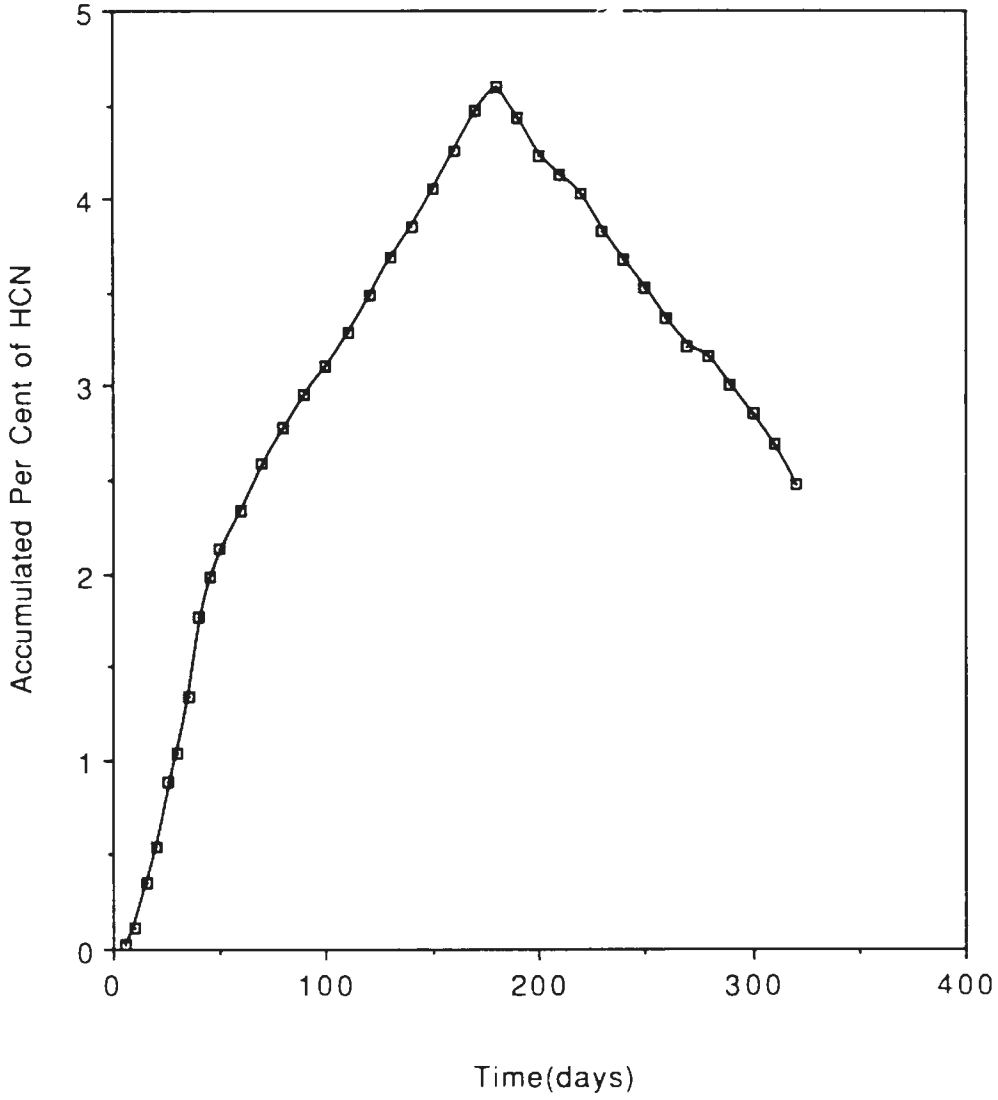


Figure 24. Per Cent of HCN Volatilized from the Second Ring(r=30.48 cm) above the Large Tank #1

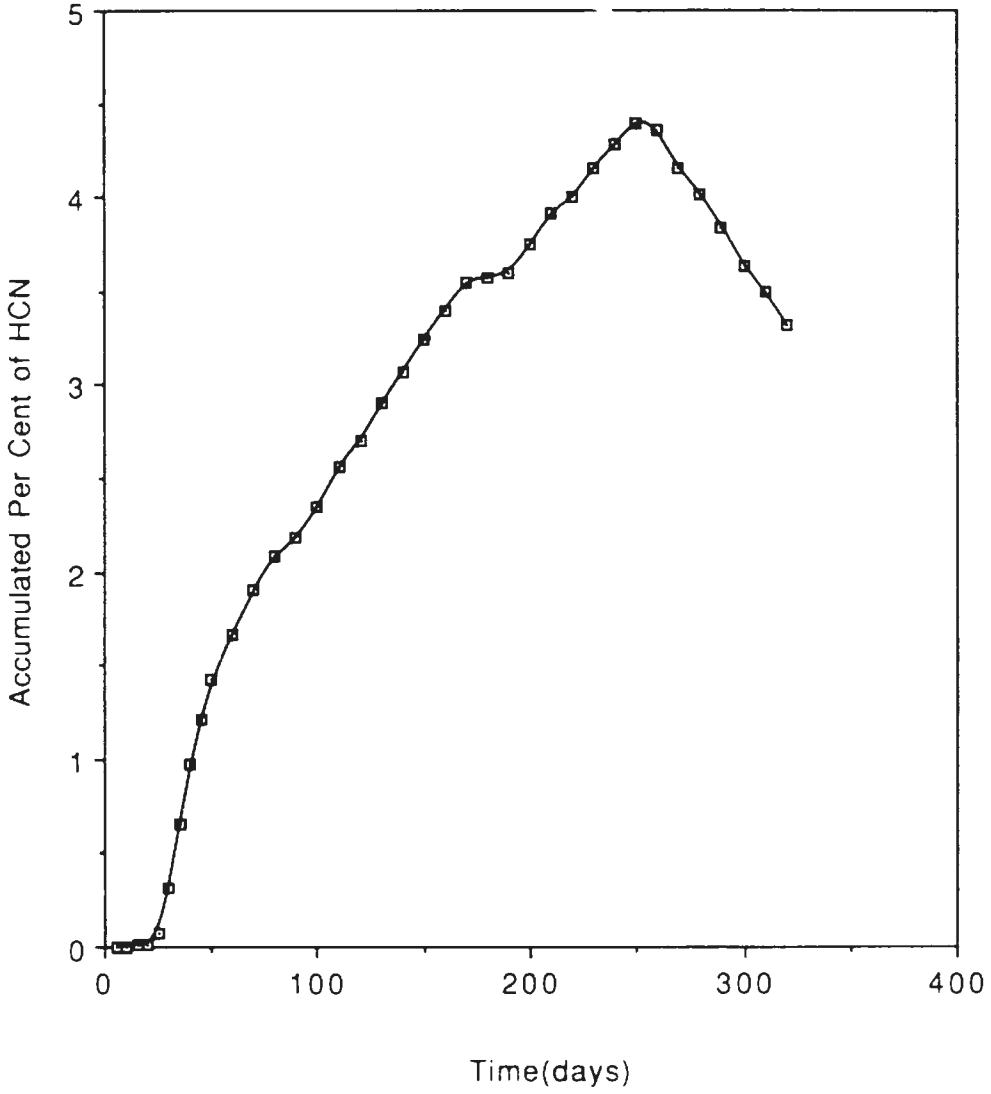


Figure 25. Per Cent of HCN Volatilized from the Third Ring(r=50.8 cm) above the Large Tank #1

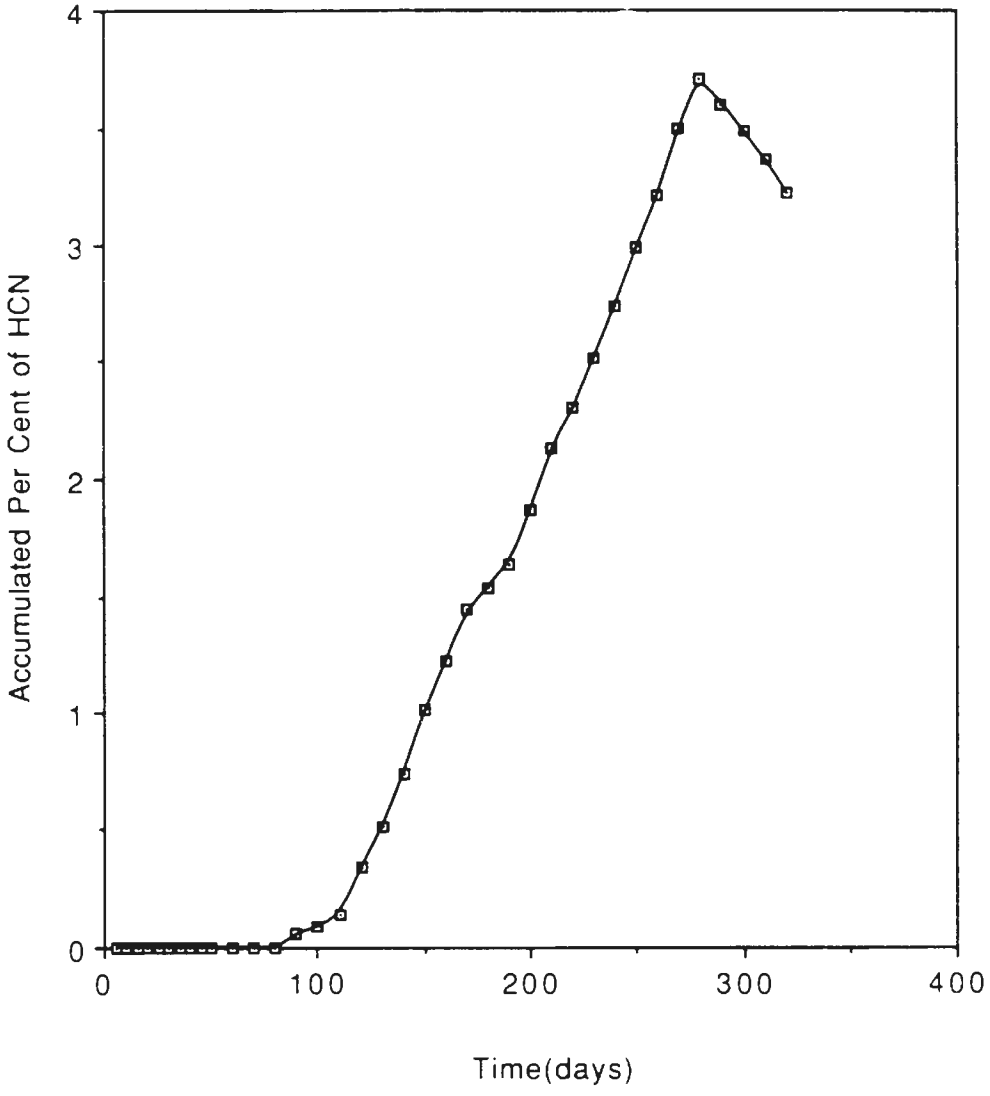


Figure 26. Per Cent of HCN Volatilized from the Fourth Ring(r=83.82 cm) above the Large Tank #1

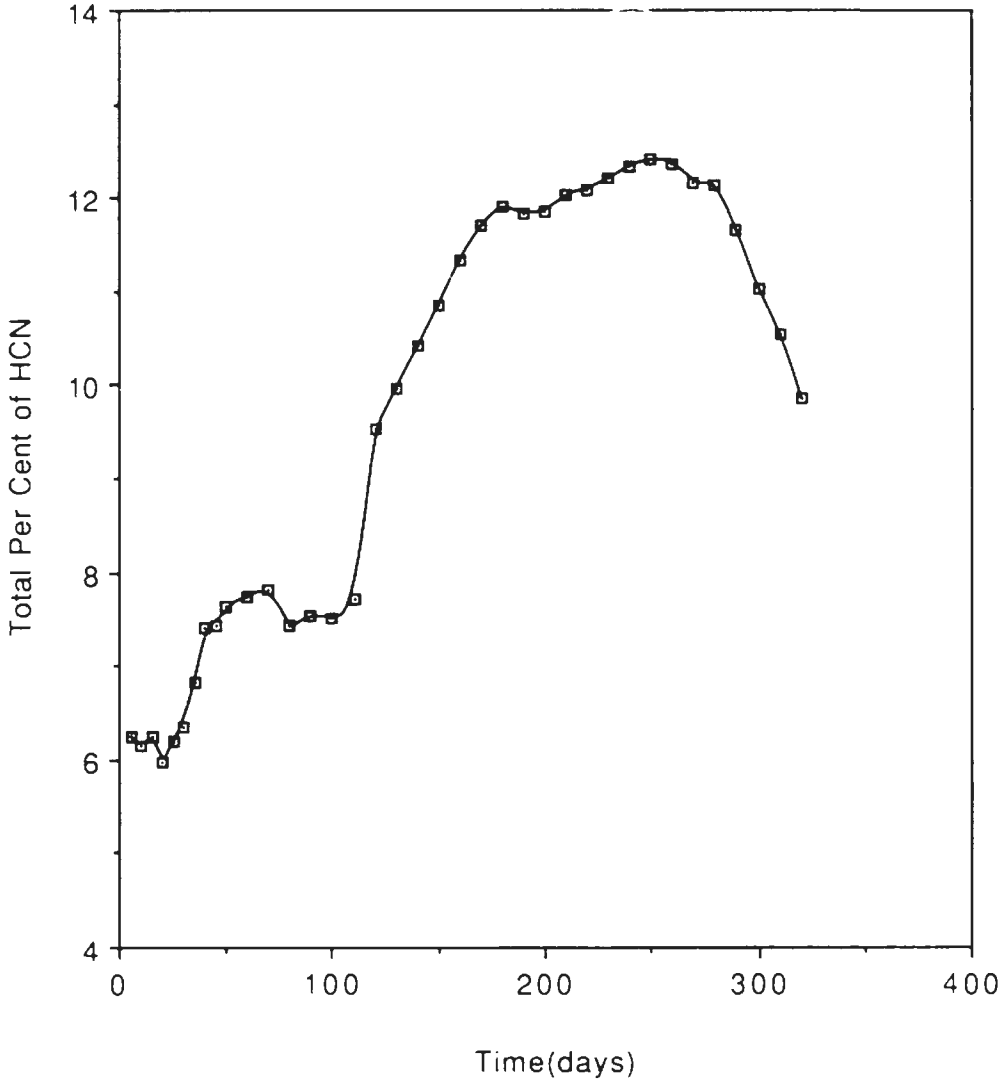


Figure 27. Total Accumulated Per Cent of HCN Volatilized above the Large Tank #1 vs Time

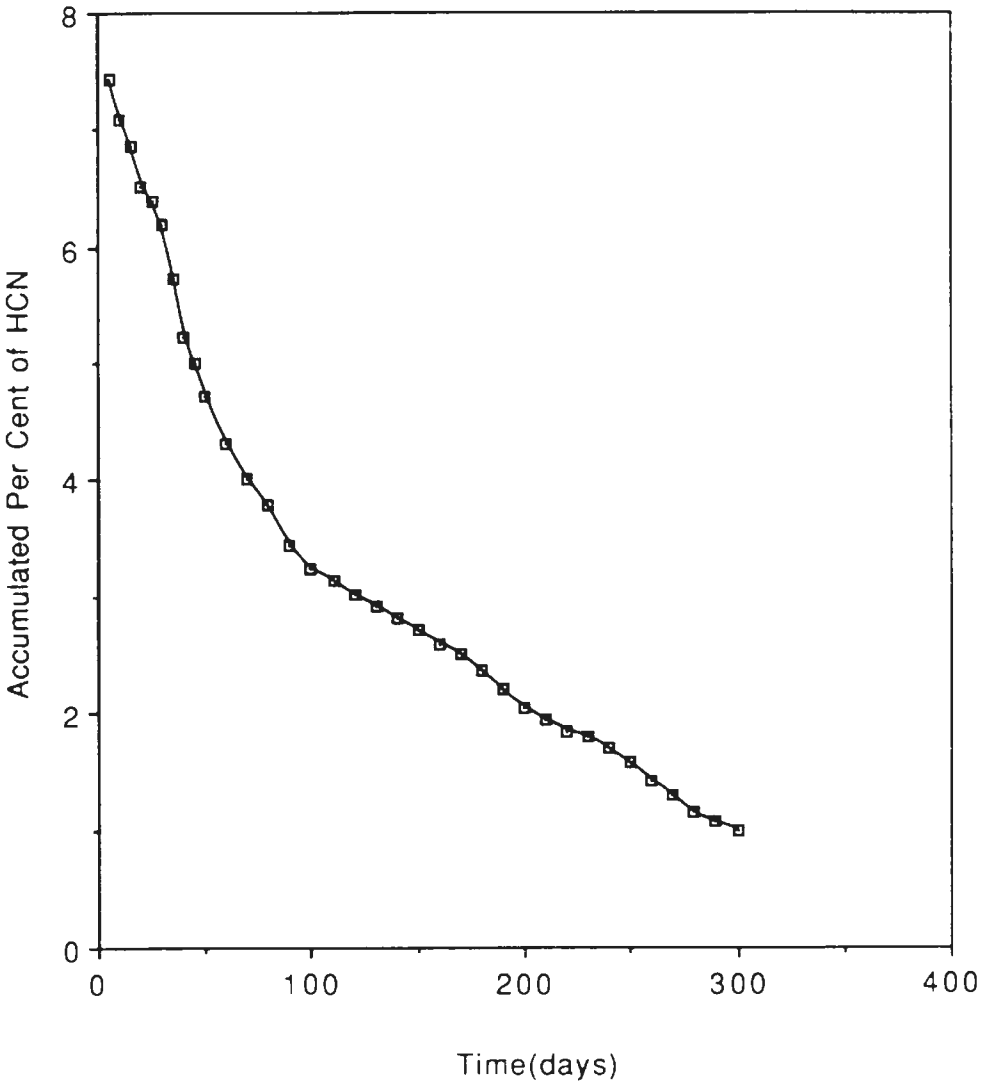


Figure 28. Per Cent of HCN Volatilized from the First Ring(r=10.16 cm) above the Large Tank #2

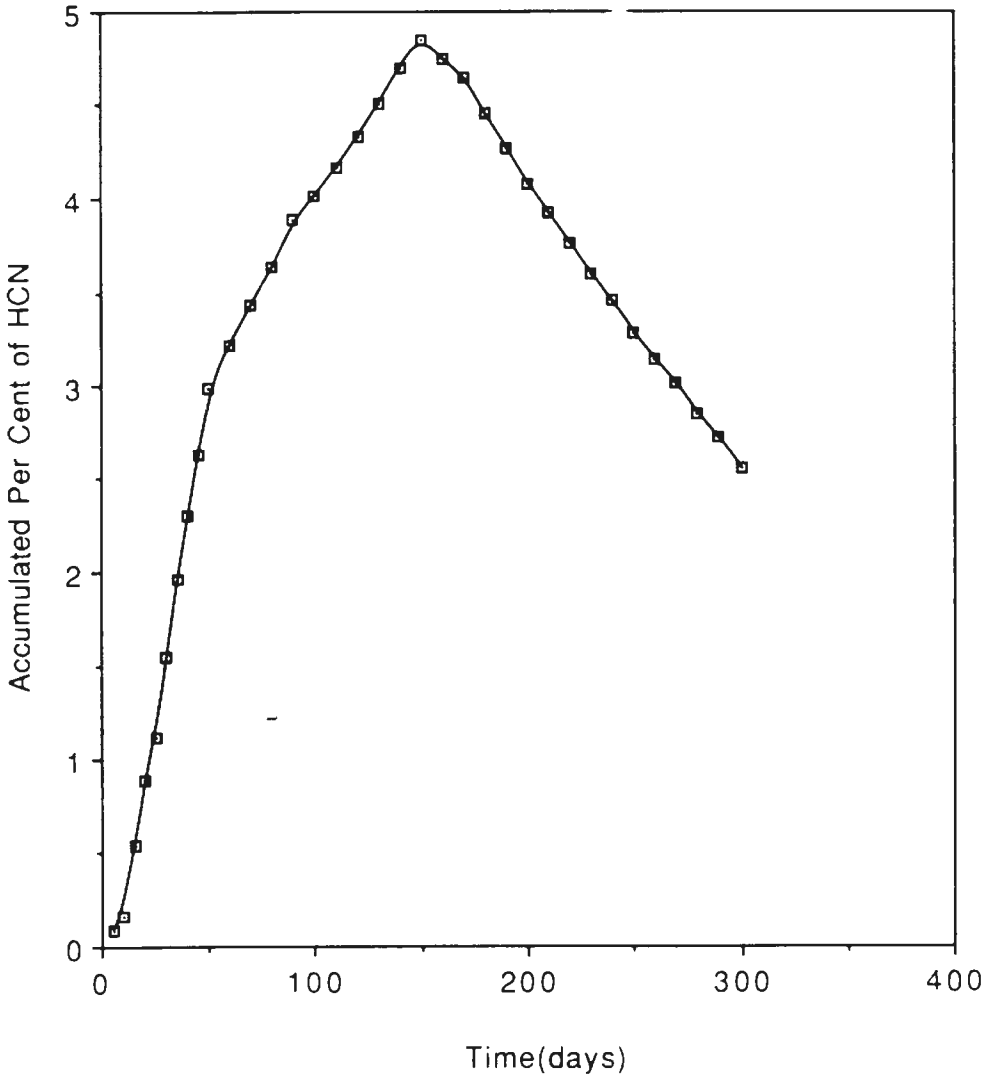


Figure 29. Per Cent of HCN Volatilized from the Second Ring(r=30.48 cm) above the Large Tank #2

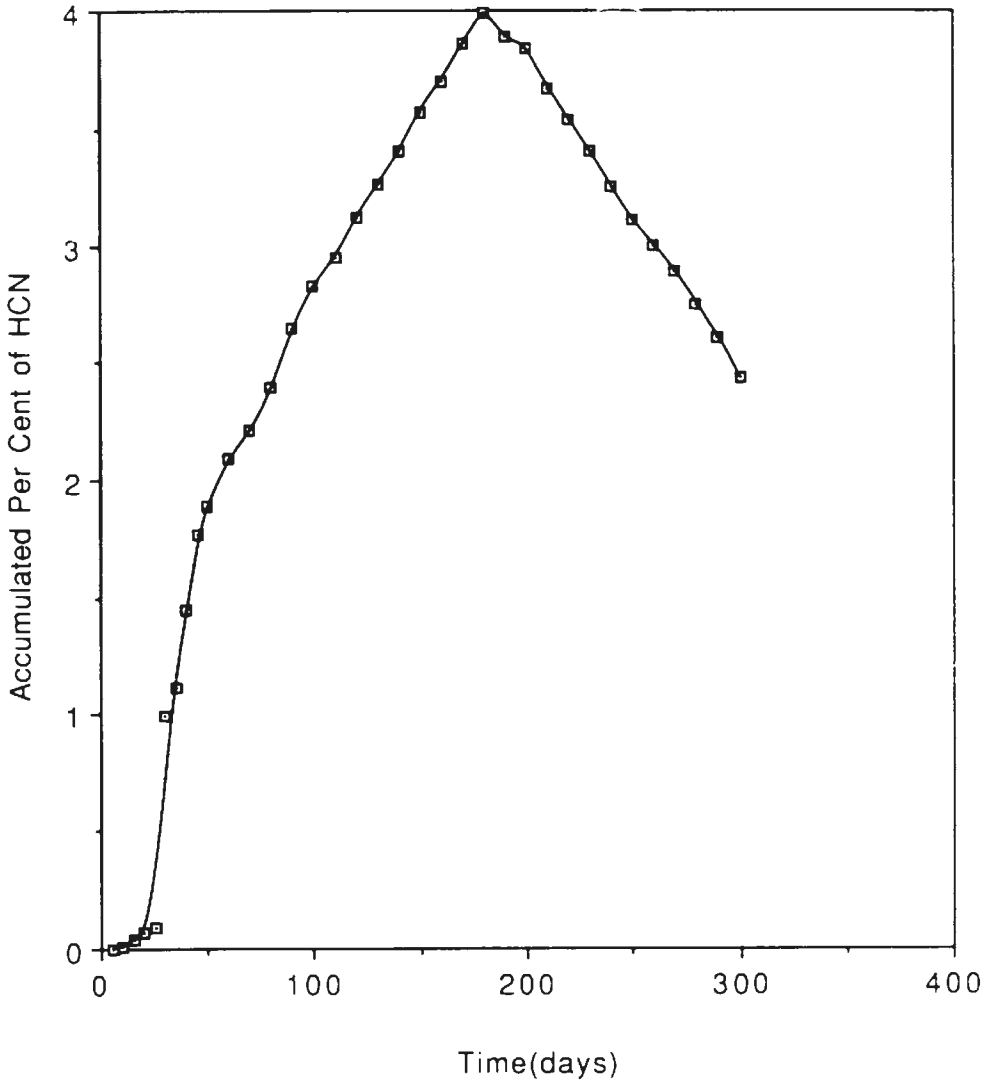


Figure 30. Per Cent of HCN Volatilized from the Third Ring(r=50.8 cm) above the Large Tank #2

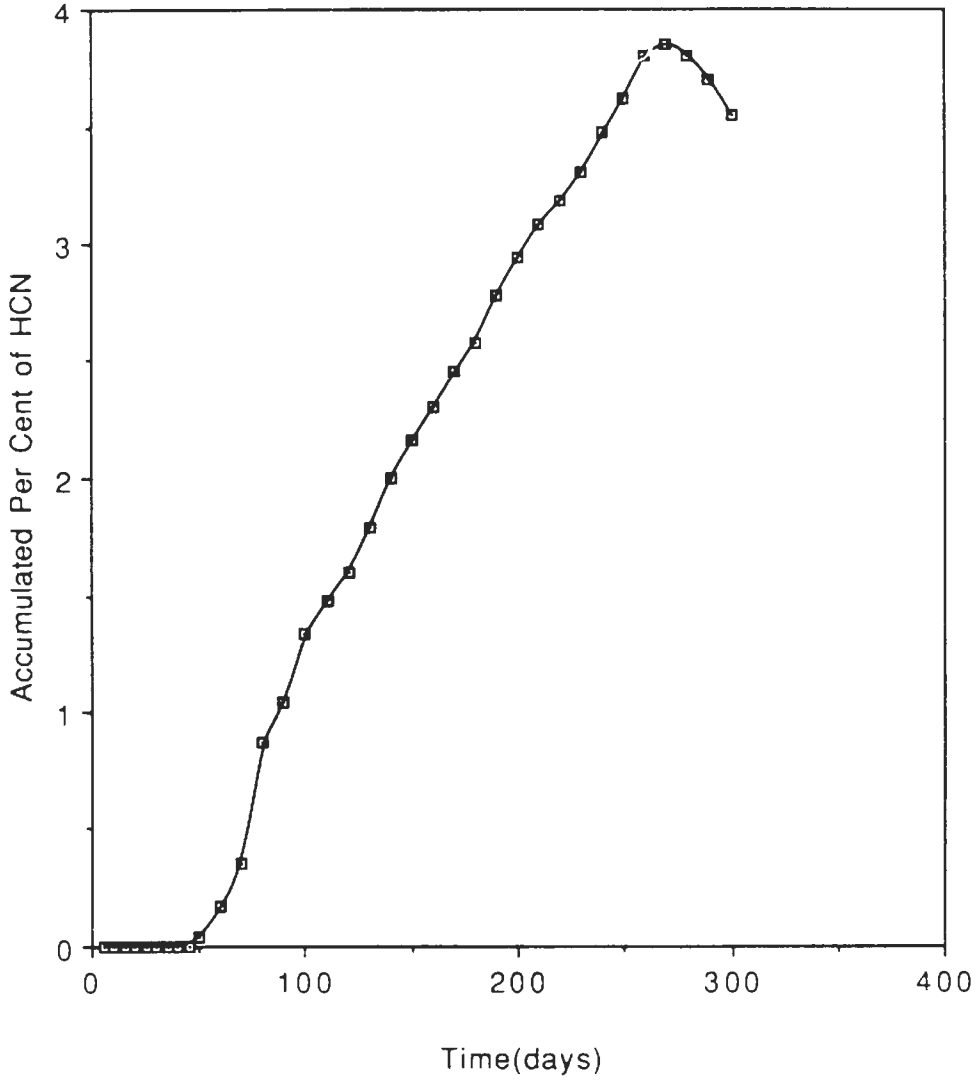


Figure 31. Per Cent of HCN Volatilized from the Fourth Ring(r=83.82 cm) above the Large Tank #2

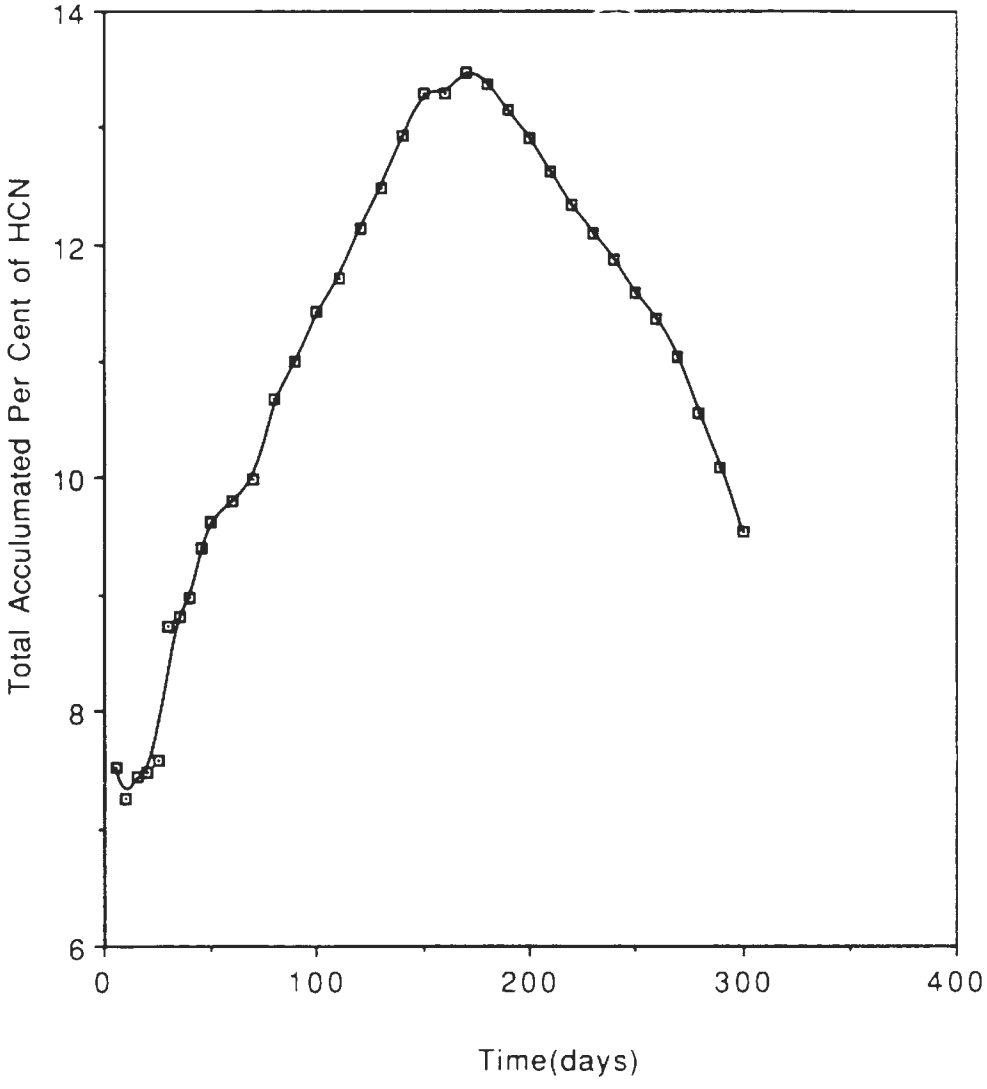


Figure 32. Total Per Cent of HCN Volatilized above the Large Tank #2 Versus Time

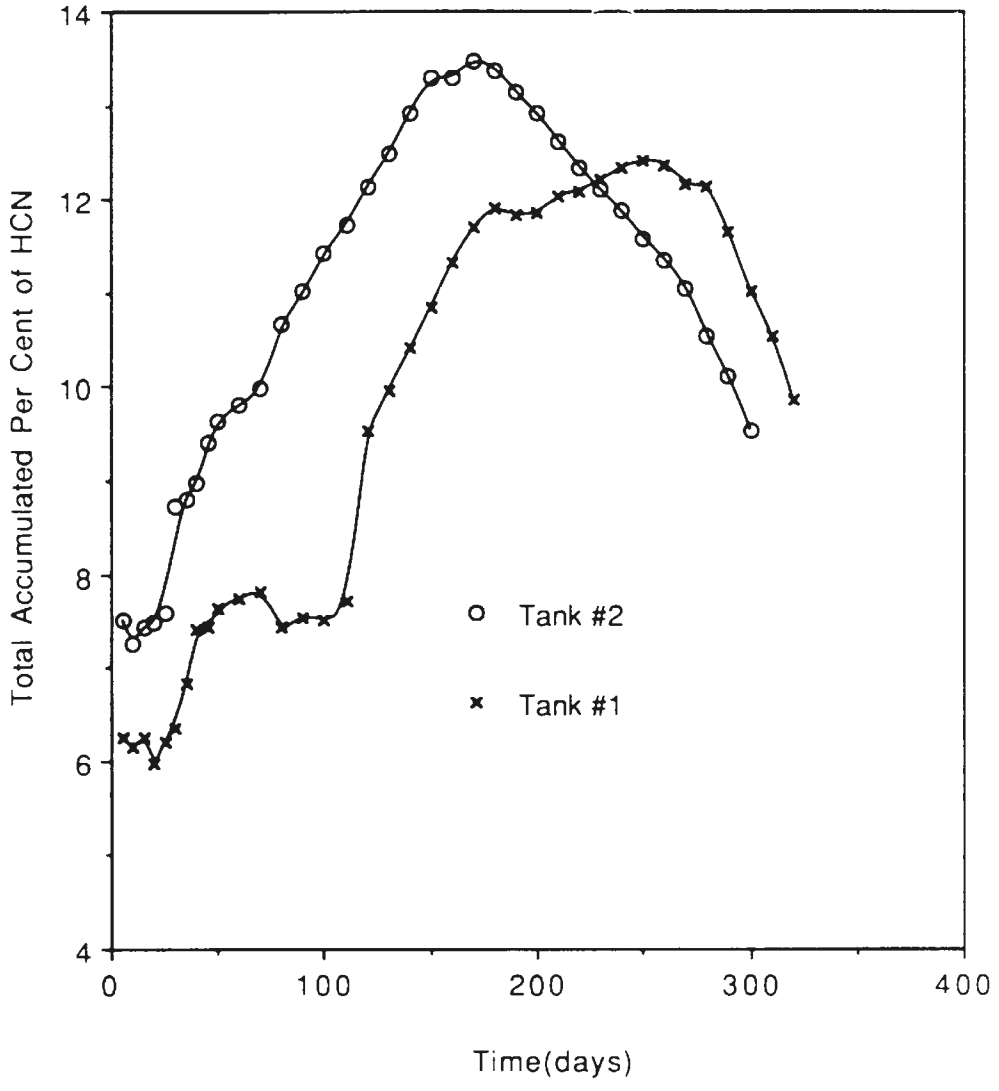


Figure 33. Total Per Cent of HCN Volatilized above Tank #1 and Tank #2 Versus Time

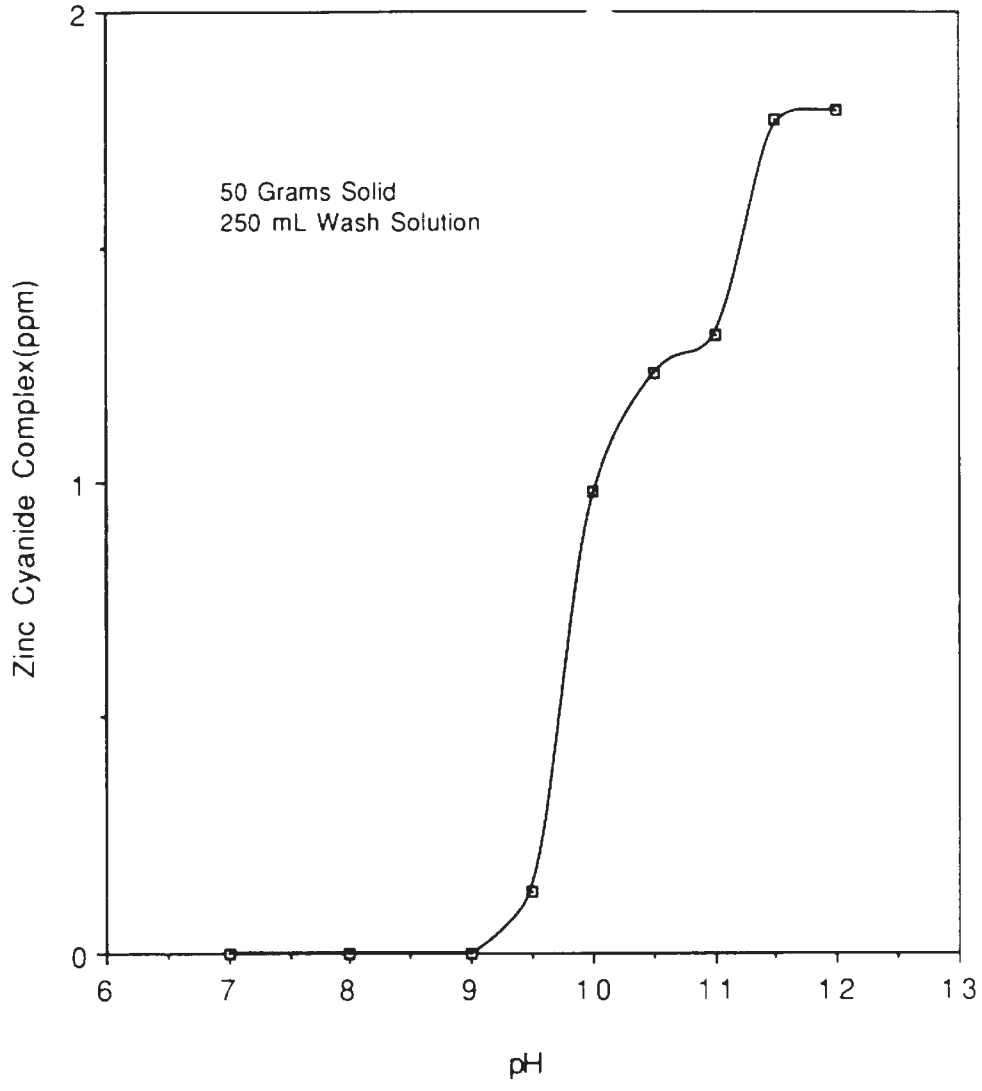


Figure 34. pH Dependence of the Zinc Cyanide Complex in the Tall Column Wash Solution

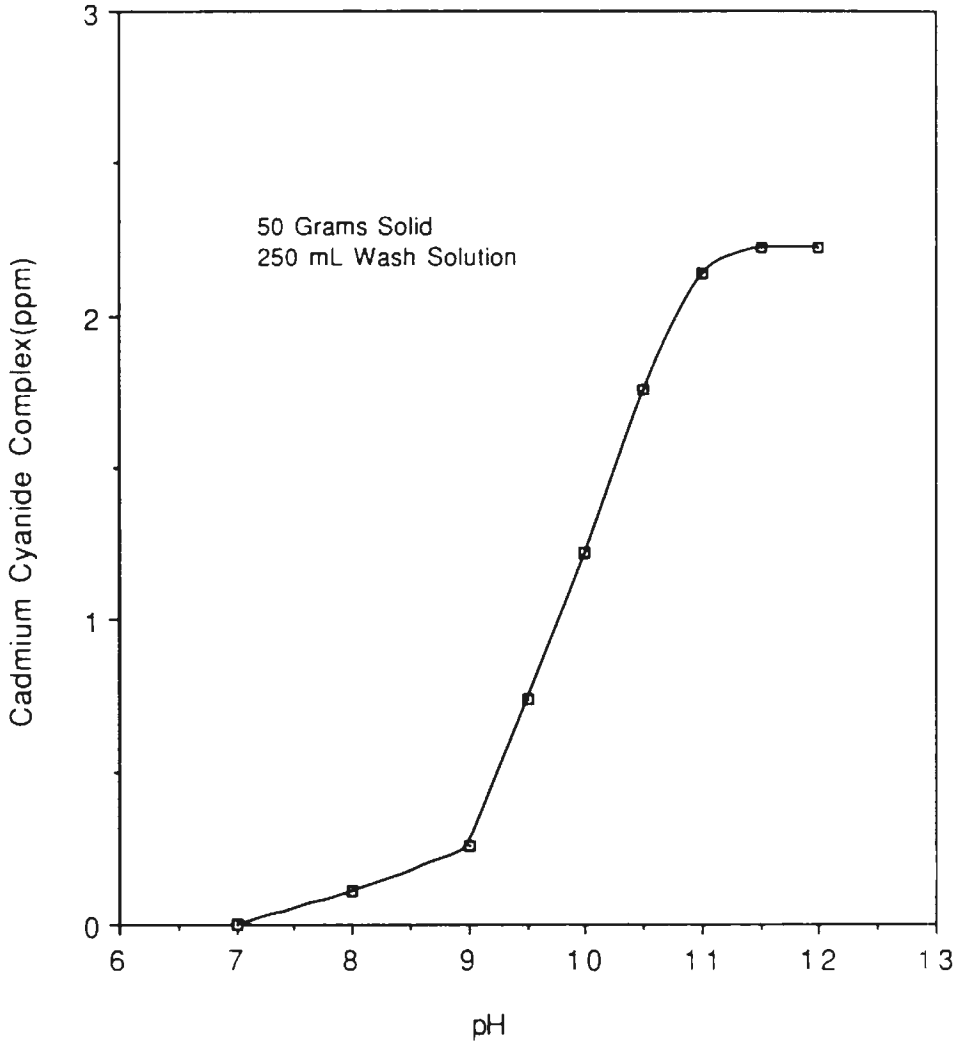


Figure 35. pH Dependence of the Cadmium Cyanide Complex in the Tall Column Wash Solution

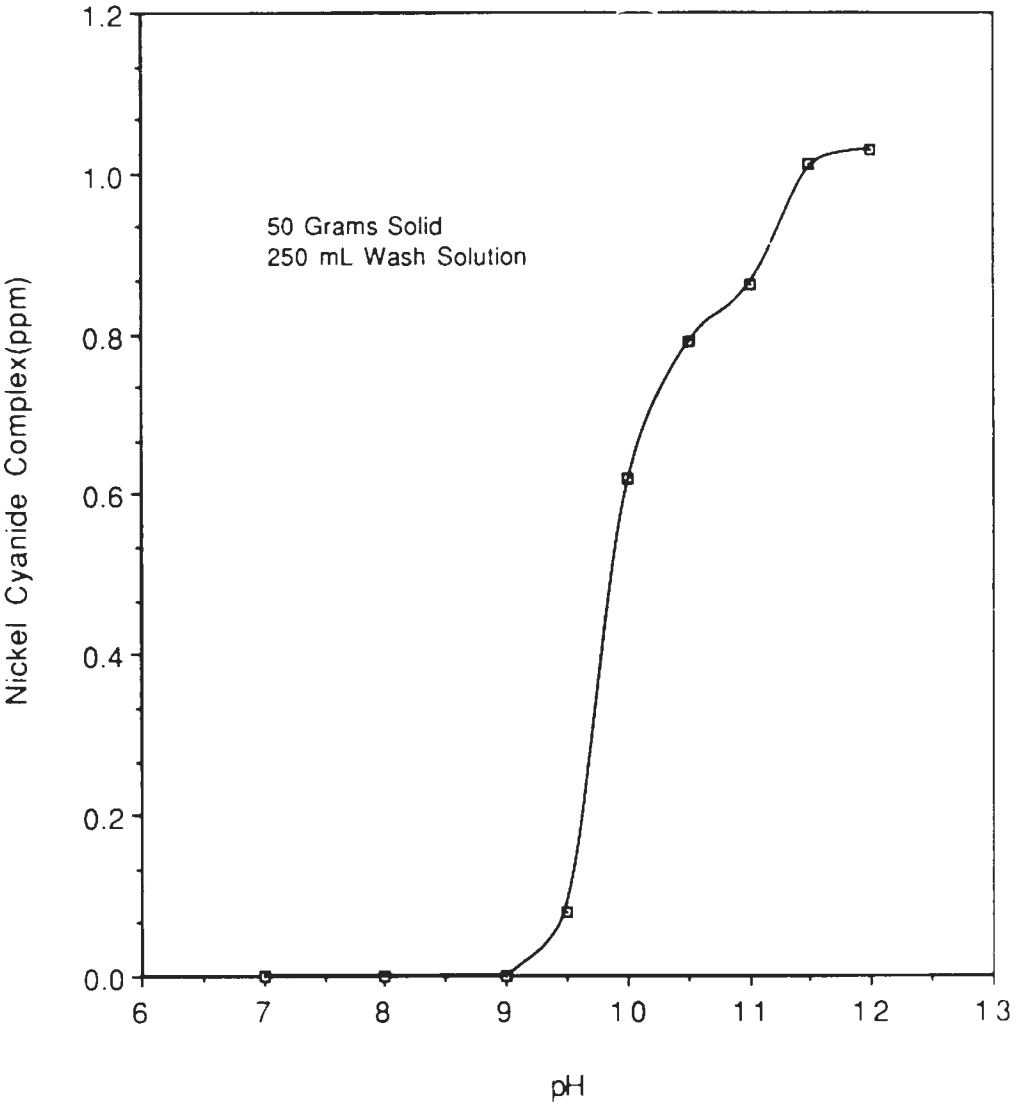


Figure 36. pH Dependence of the Nickel Cyanide Complex in the Tall Column Wash Solution

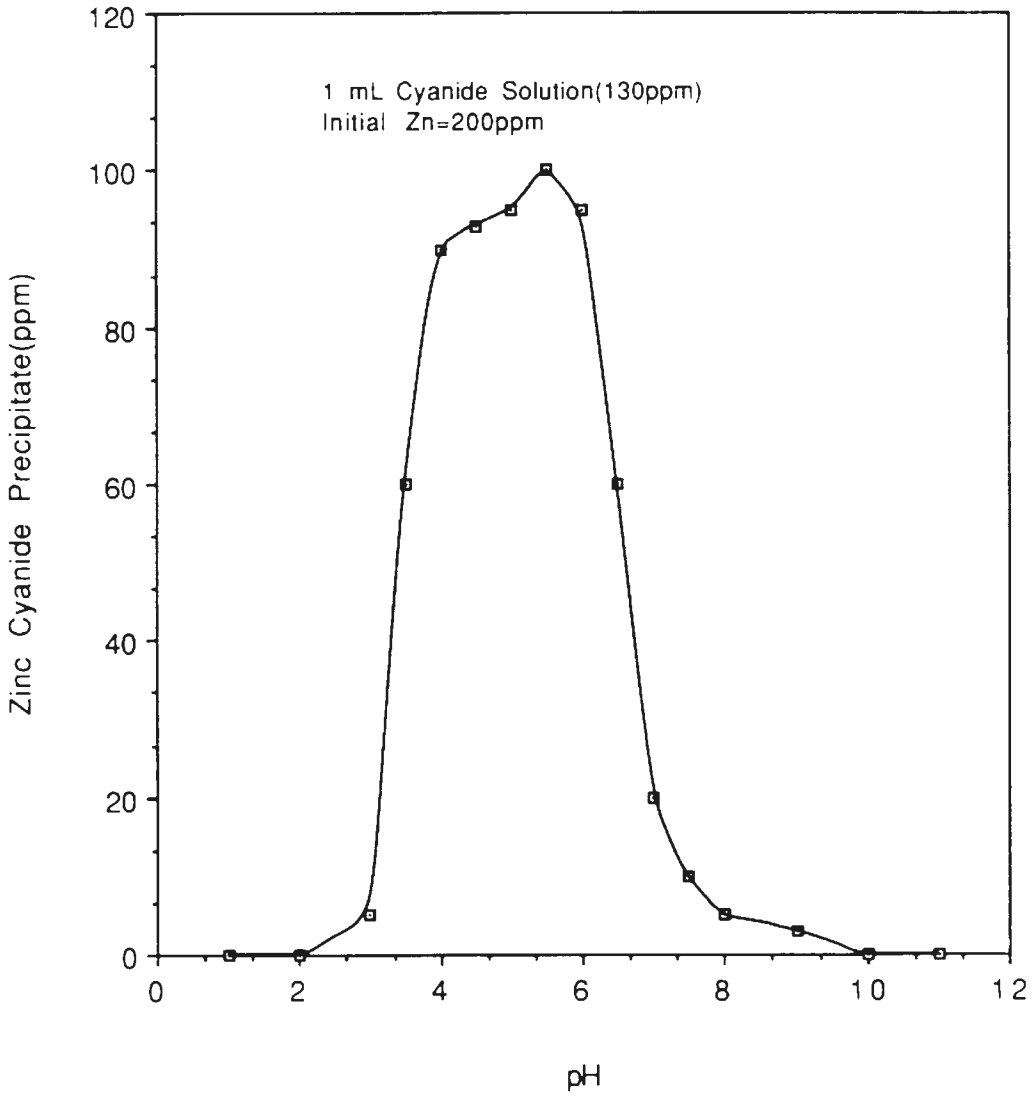


Figure 37. Effect of pH on the Concentration of Zinc Cyanide Precipitate in Cyanide Solution In a Stirred Batch Reactor Test

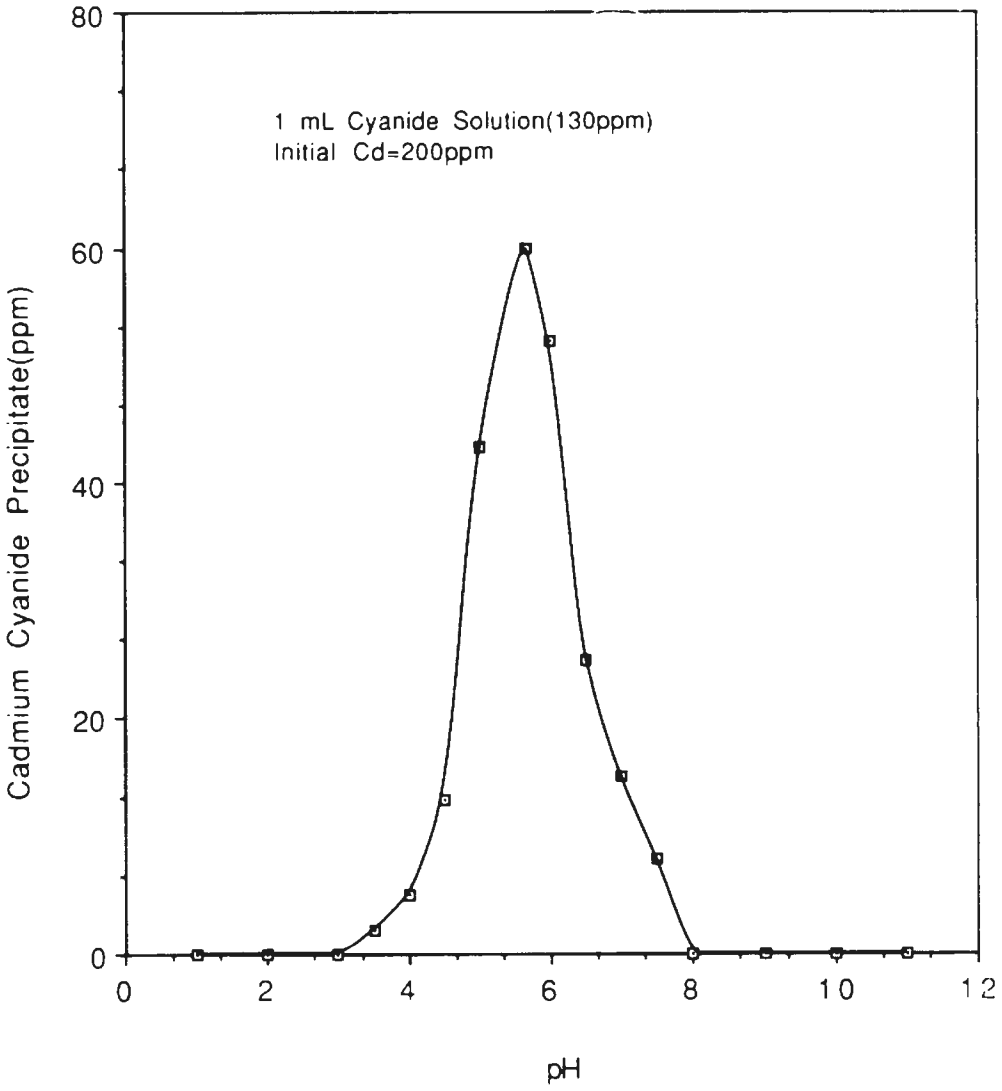


Figure 38. Effect of pH on the Concentration of Cadmium Cyanide Precipitate in Cyanide Solution in a Stirred Batch Reactor

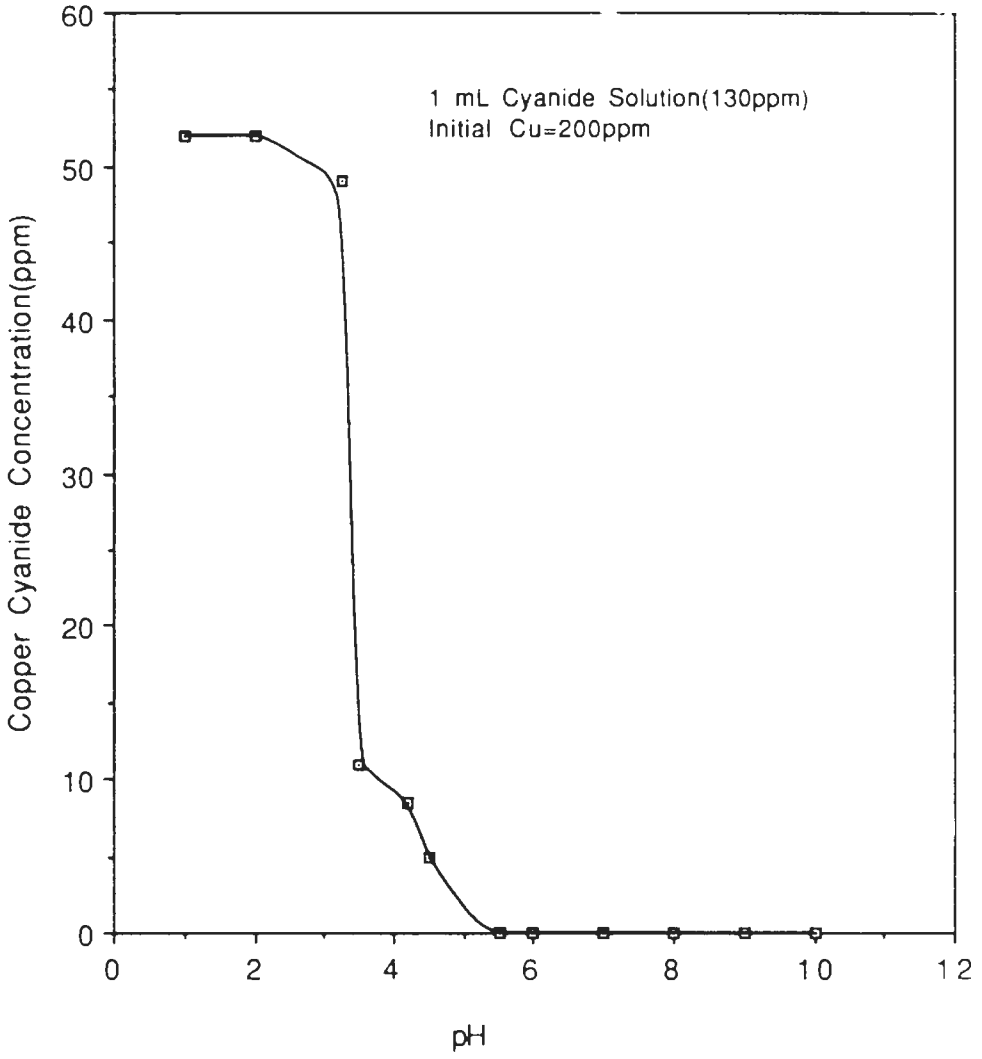


Figure 39. Effect of pH on the Concentration of Copper Cyanide Precipitate in Cyanide Solution in a Stirred Batch Reactor

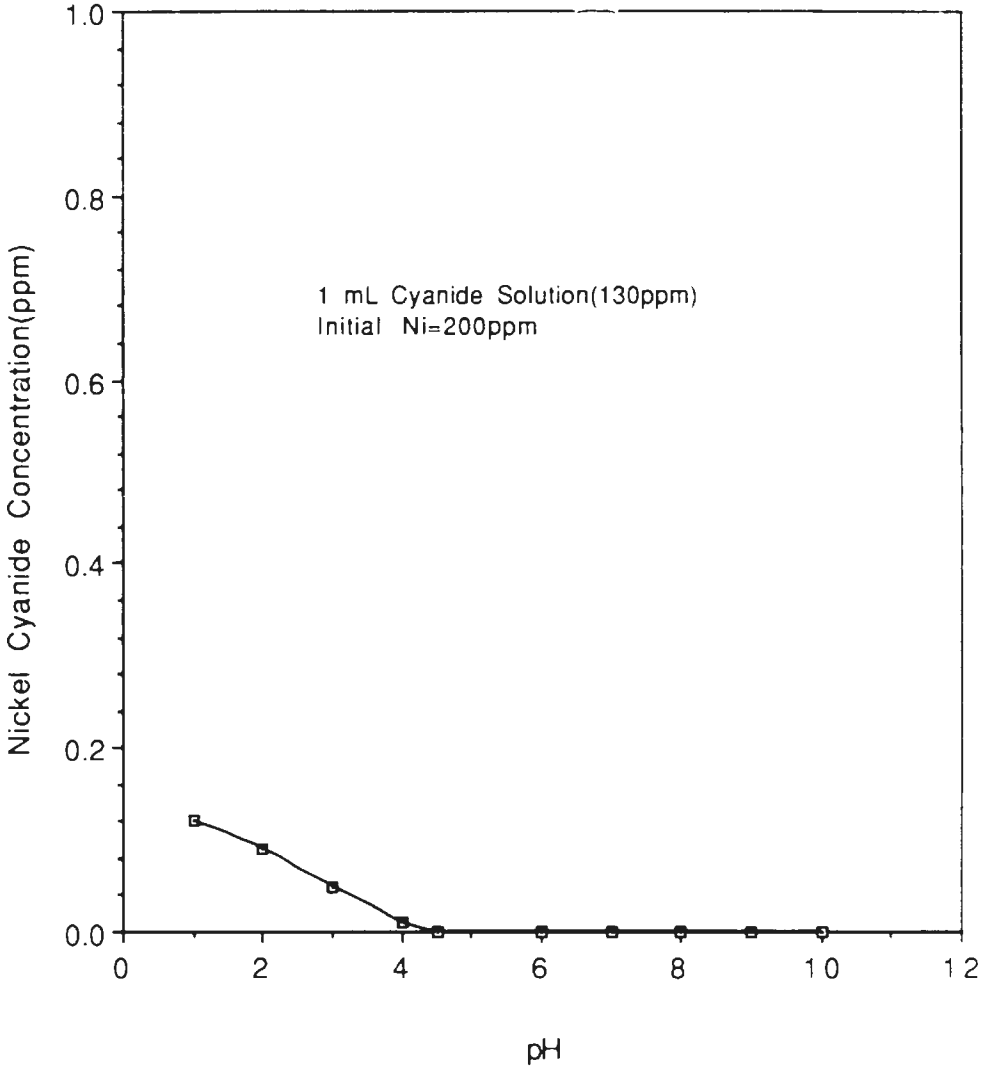


Figure 40. Effect of pH on the Concentration of Nickel Cyanide Precipitate in Cyanide Solution in a Stirred Batch Reactor

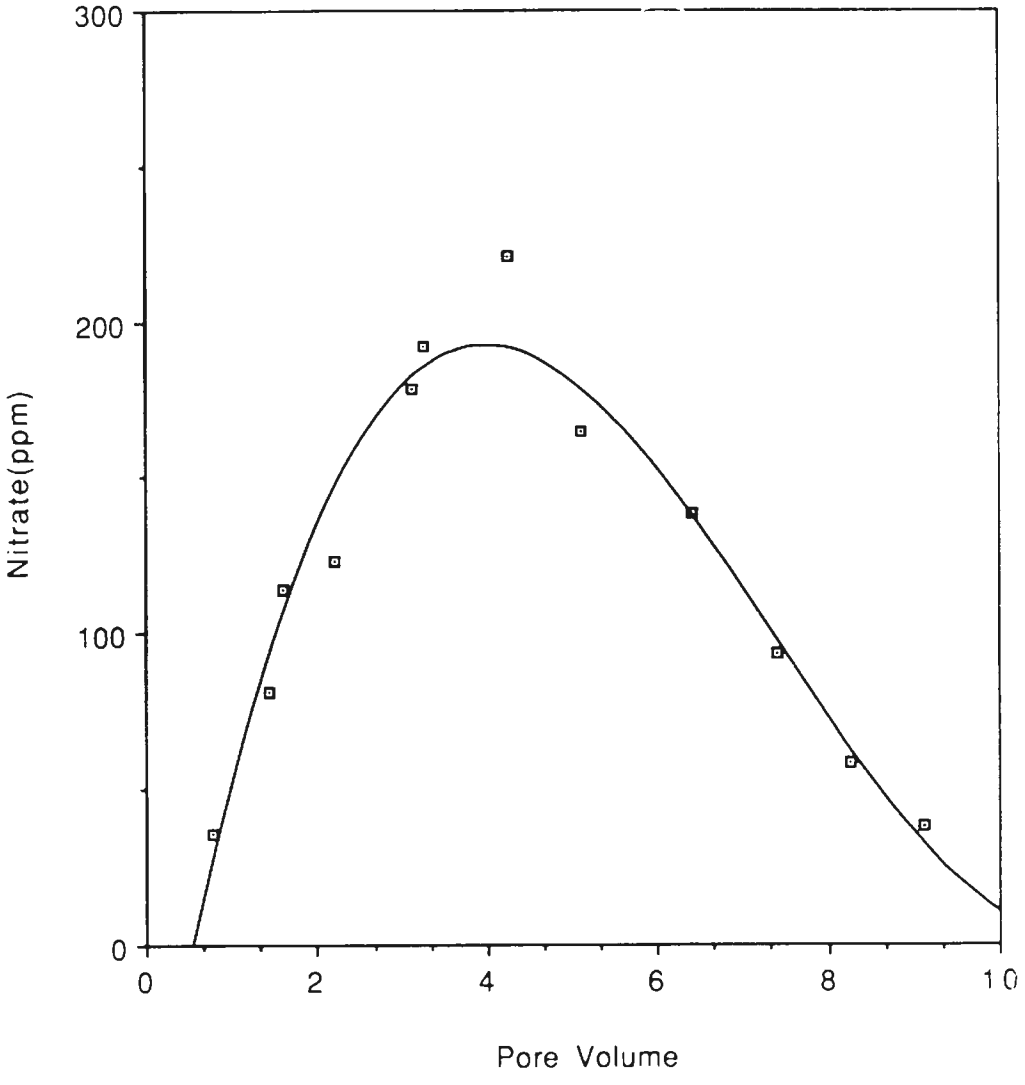


Figure 41. Concentration of Nitrate in the Effluent Versus Pore Volume for the Tall Column Test

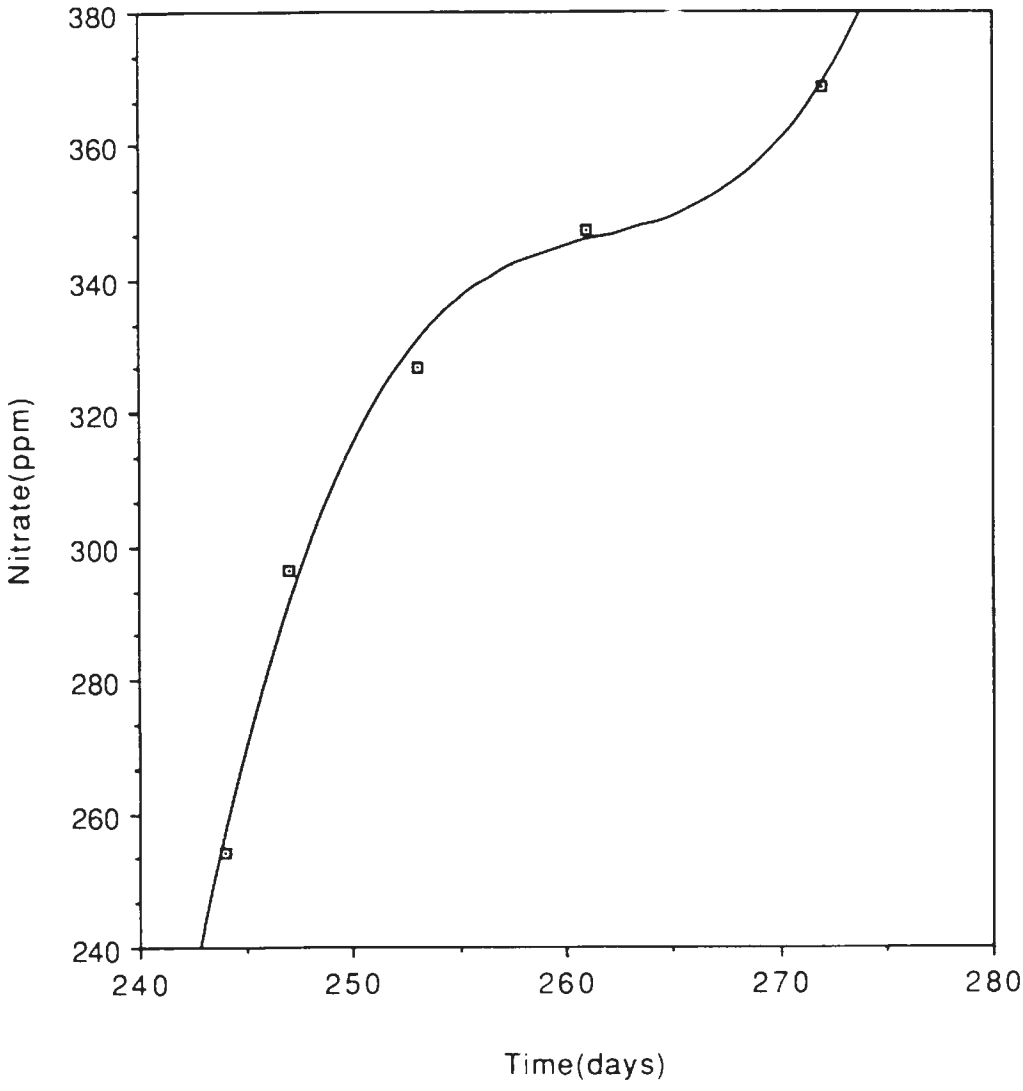


Figure 42. Concentration of Nitrate in the Effluent Versus Time for the Large Tank #2 Test

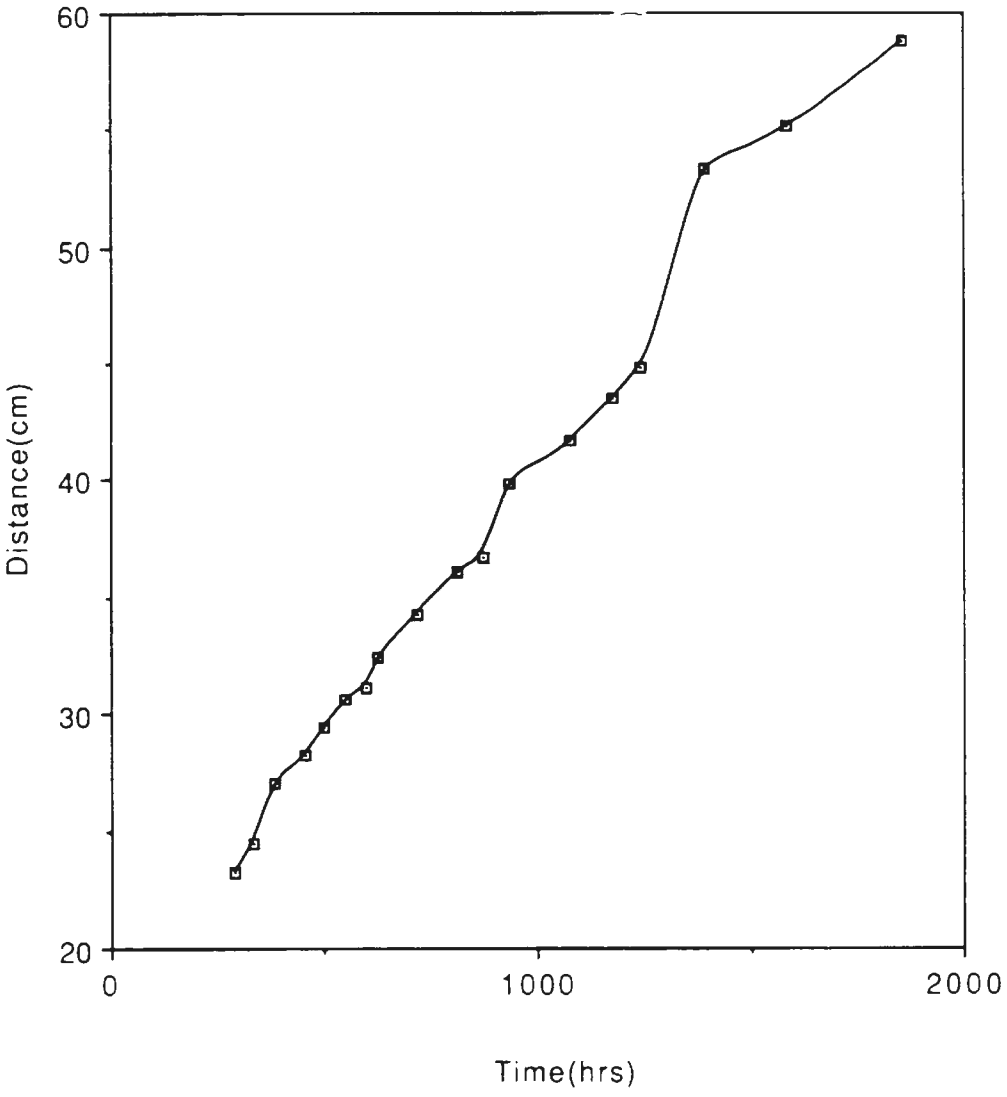


Figure 43. Advancement of the Wet Front Horizontally Versus Time for the Large Tank #1 Test

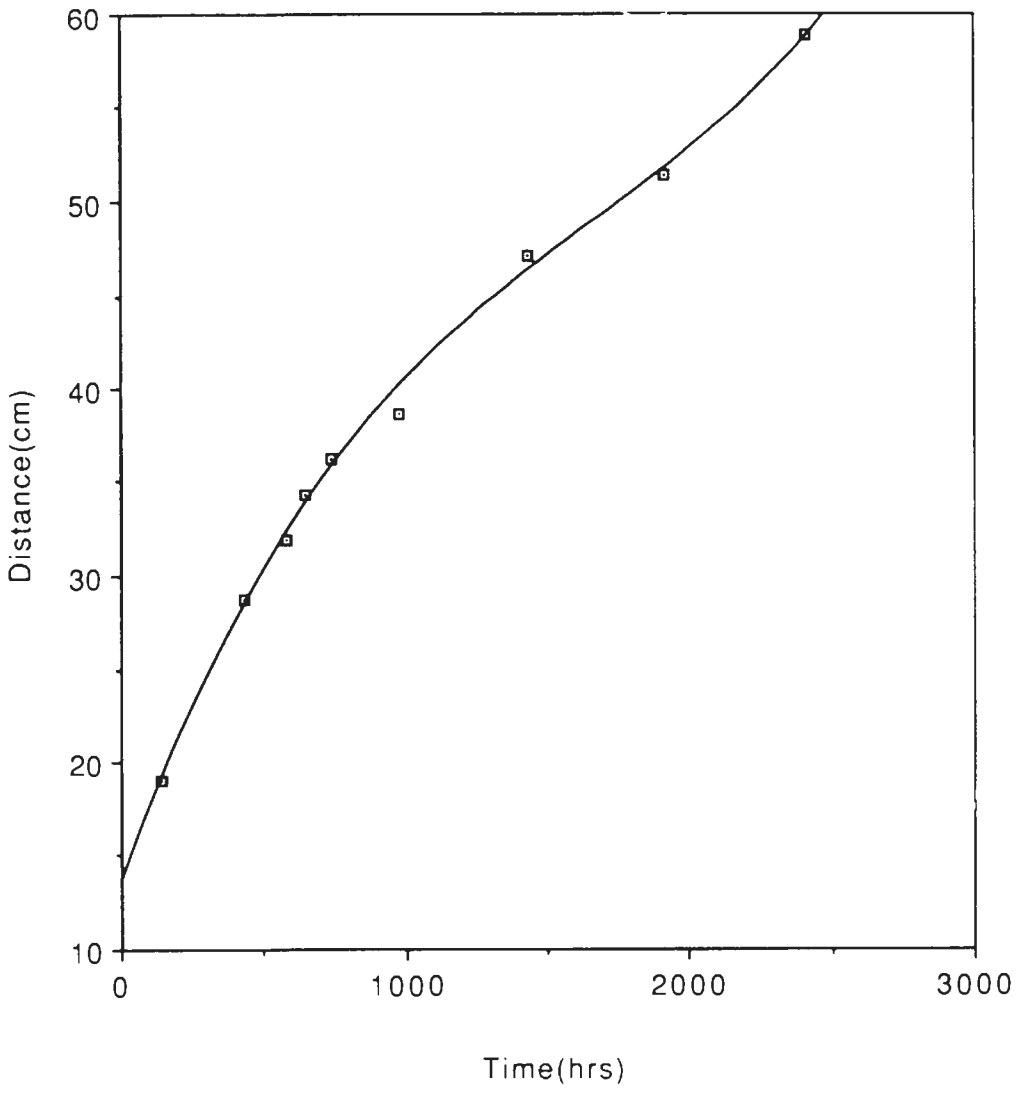


Figure 44. Advancement of the Wet Front Horizontally Versus Time for the Large Tank #2 Test

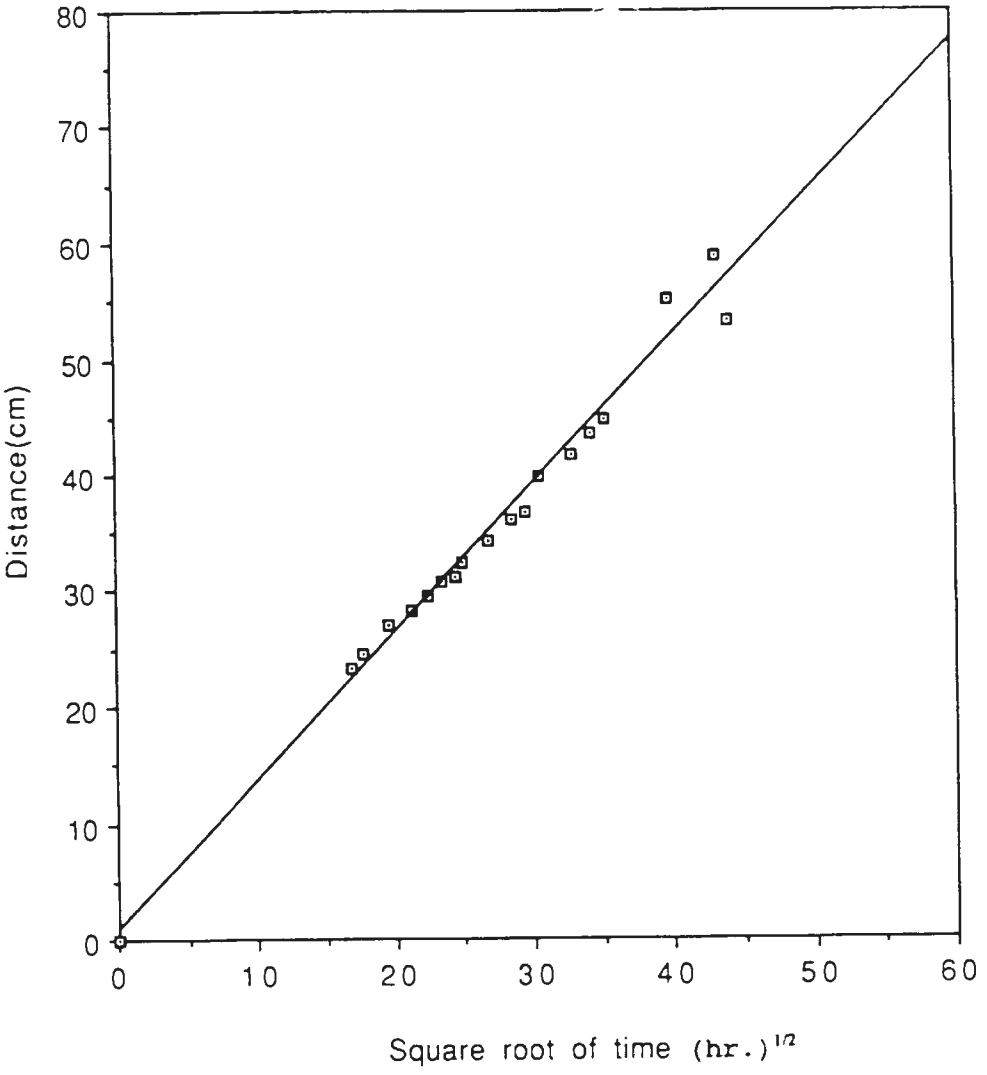


Figure 45. Advancement of the Wet Front Horizontally Versus Square Root of Time for the Large Tank #1 Test

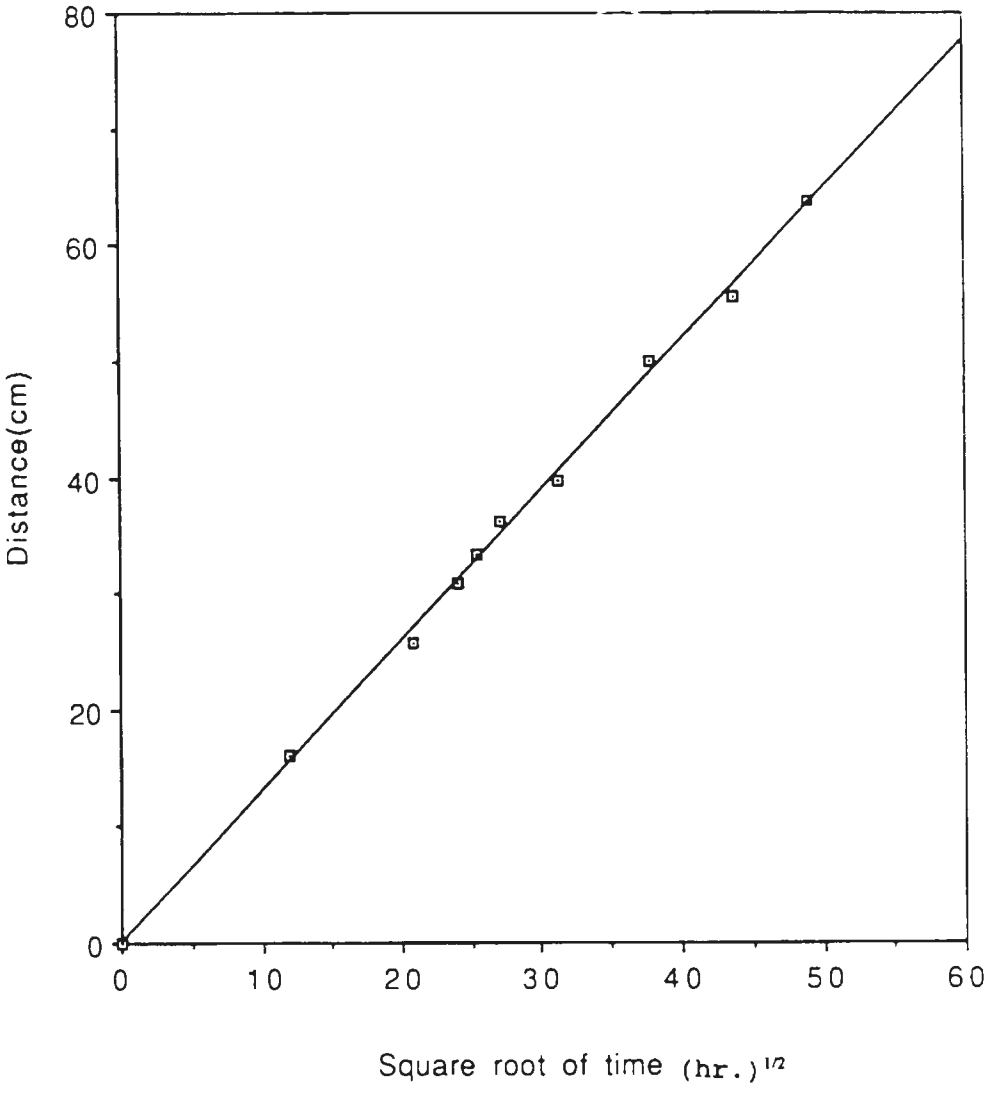


Figure 46. Advancement of the Wet Front Horizontally Versus Square Root of Time for the Large Tank #2 Test